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Environmental Pollution Control Alternatives
Economics of Wastewater Treatment
Alternatives for the Electroplating Industry

Centec Corp., Reston, VA

Prepared for

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June 1979

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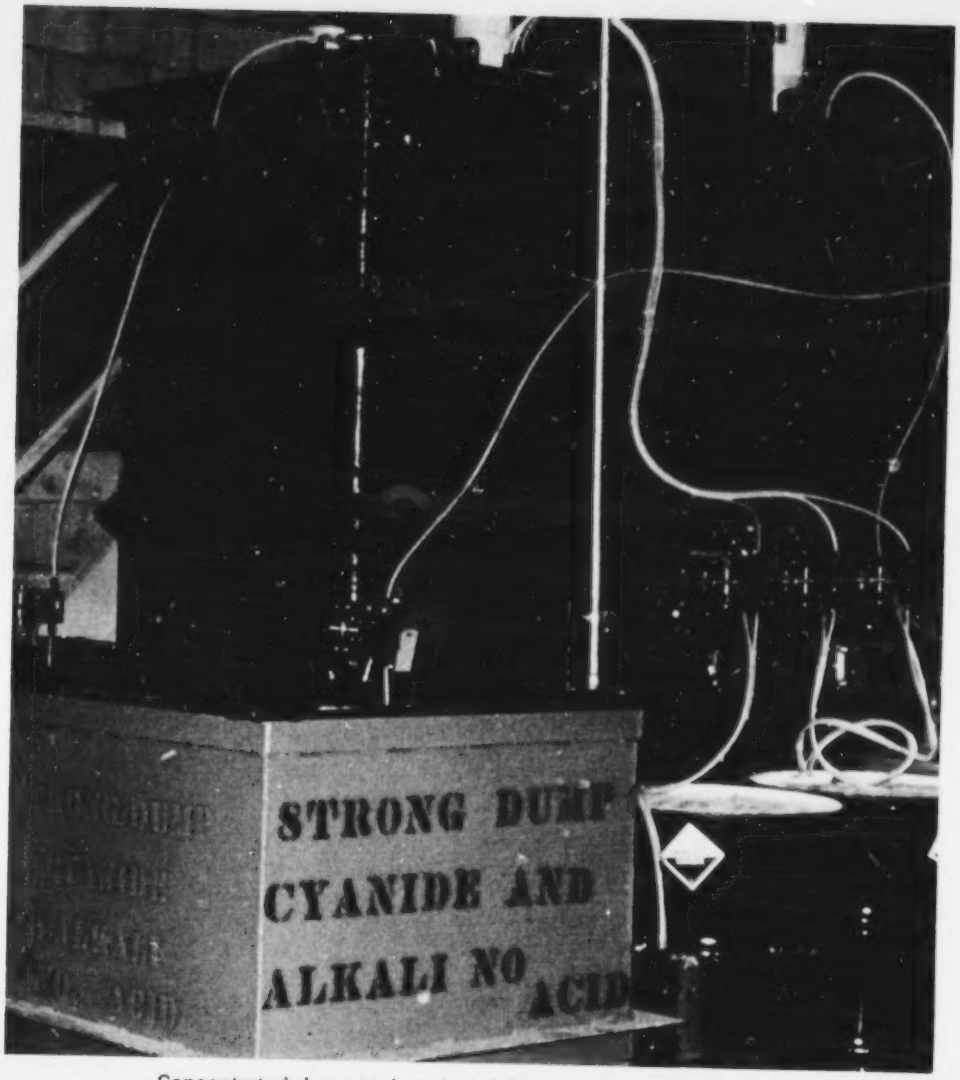

Concentrated dump tank and modular cyanide oxidation and neutralization/flocculation units

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This report addresses the economics of wastewater treatment alternatives as a guide for minimizing the costs of meeting water pollution control requirements. Initially, operating and investment costs are presented for conventional wastewater treatment systems employed by the electroplating industry. These systems are then compared with alternative technologies that may offer cost savings. Finally, modifications capable of reducing raw material use and pollution costs are described.

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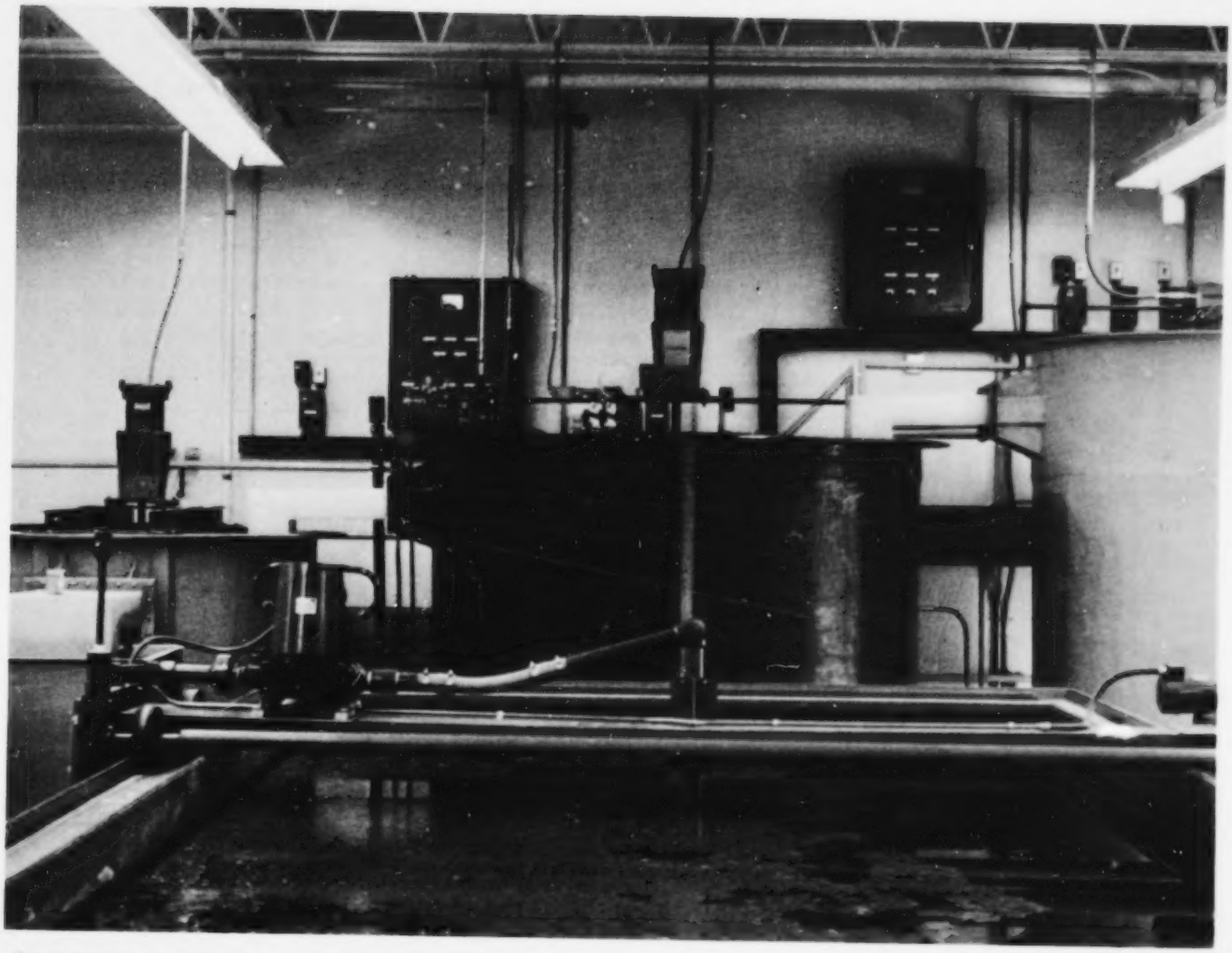


Pretreatment, neutralization, and flocculation tanks with clarifier/thickener

1. Overview

The Water Pollution Control Act Amendments (Public Law 92-500), enacted in 1972, required a base level of removal for pollutants being discharged by industry to waterways or public treatment systems. The Clean Water Act of 1977 (Public Law 95-217) granted the Environmental Protection Agency (EPA) additional regulatory powers to set effluent standards and to prohibit the presence of specified toxic chemicals in wastewater discharged to waterways or to publicly owned treatment works (POTW). Industrial pollutants that are discharged to POTW's and thereby reduce plant efficiency or contaminate plant sludge will be regulated. The EPA is identifying the toxic materials to be covered by the regulations. The Resource Conservation and Recovery Act of 1976 (Public Law 94-580) will regulate the disposal of industrial sludges containing toxic materials.

Costs of meeting the pollution control requirements of these Federal laws, combined with the rising costs of energy, raw materials, and chemicals, can greatly affect operating costs in the electroplating industry. The raw materials typically found in electroplating wastewater as well as the costs of those materials and of wastewater treatment chemicals, utilities, and sewer fees are shown in Table 1.

Common electroplating chemicals, such as cyanide, chromium, nickel, cadmium, and zinc, already are classified as toxic substances. Moreover, the costs of these chemicals and of utilities have risen from 50 to 150 percent since 1972. The changes in prices and regulations dictate that the economics and technologies for water pollution control be reevaluated and that methods for improving raw material yields be analyzed. In some cases, in-plant changes, proper selection of pollution control or recovery technologies, and reduction in wastewater flow rates can improve operating costs while reducing or eliminating discharge of toxic pollutants.

This report addresses the economics for the foregoing techniques as a guide for minimizing the costs of meeting water pollution control requirements. Initially, operating and investment costs are presented for conventional wastewater treatment systems employed by the electroplating industry. These systems are then compared with alternative treatment technologies that may offer cost savings. Finally, modifications capable of reducing raw material use and pollution control costs are described.

Table 1.

Raw Material, Pollutant Control Chemicals, and Utilities Used by the Electroplating Industry

Item	1972 cost	1978 cost
Plating chemicals ($/lb):[a,b]		
Boric acid (H_3BO_3)	0.069	0.176
Cadmium chloride ($CdCl_2$)[c]	—	2.60
Chromic acid (H_2CrO_4)[c]	0.37	0.78
Copper cyanide ($Cu(CN)_2$)[c]	1.05	1.95
Copper sulfate ($CuSO_4$)[c]	0.47	0.88
Nickel chloride ($NiCl_2$)[c]	0.67	1.04
Nickel sulfate ($NiSO_4$)[c]	0.50	0.76
Sodium cyanide ($NaCN$)[c]	0.21	0.40
Zinc (as Zn metal)[c]	0.18	0.31
Zinc cyanide ($Zn(CN)_2$)[c]	0.64	1.41
Water pollution control chemicals ($/lb):[a,b]		
Calcium hydroxide ($Ca(OH)_2$)	0.010	0.017
Calcium oxide (CaO) quicklime	0.009	0.016
Chlorine (Cl_2)	0.038	0.075
Ferrous sulfide (FeS)	—	0.40
Hydrochloric acid (28% HCl)	0.0135	0.023
Sodium bisulfite ($NaHSO_3$)	0.066	0.13
Sodium carbonate (58% Na_2CO_3)	0.018	0.03
Sodium hydroxide (98% NaOH equivalent)	0.036	0.08
Sodium hypochlorite (NaOCl)	—	0.40
Sodium sulfide (Na_2S)	0.07	0.12
Sulfur dioxide (SO_2)	0.038	0.085
Sulfuric acid (H_2SO_4)	0.017	0.023
Utilities:[d]		
Electricity ($/kWh)	0.028	0.045
Steam by energy source ($/$10^6$ Btu):		
Natural gas	1.03	2.07
Oil	1.39	3.53
Water ($/1,000 gal):		
Use fee	0.25	0.50
Sewer fee[e]	0.25	0.60

[a]Prices are for bulk shipments of chemicals; prices for smaller quantities or especially packaged quantities may be 10% to 50% higher. Plating chemicals purchased with proprietary additives are from 20% to 40% higher.

[b]Prices from *Chemical Marketing Reporter*, Oct. 30, 1972, and Feb. 20, 1978.

[c]Substance is on list of EPA's 131 priority pollutants.

[d]Average prices.

[e]Typical of a metropolitan area.

2. Costs of Conventional Wastewater Treatment Systems

Introduction

Treatment of metal finishing wastes by neutralization followed by gravity settling for separation of suspended solids—with additional treatment steps for hexavalent chromium and cyanide—has become so widely used in the metal finishing industry that it is usually referred to as "conventional" treatment. Figure 1 is a schematic of a conventional treatment facility for electroplating wastes containing chromium and cyanides in addition to other heavy metals, acids, and alkalis.

The purpose of this section is to provide guidance to the plater in estimating the cost of installing and operating these systems in an electroplating facility. Predicting the performance of any treatment system requires laboratory testing to simulate its operation on the intended feed material. Based on the test results, the ability of the system to bring a discharge into compliance with the environmental control regulation can be ascertained.

Excellent advice on conducting the in-plant evaluation leading to the final sizing of waste treatment equipment is available in several publications listed in the bibliography. Detailed guidance in minimizing the cost of wastewater treatment techniques is given in Section 4. One major precaution stands out so strongly as a factor in improper selection of equipment, however, that it deserves a brief discussion before the cost of treatment equipment is estimated.

Pollutant loading on a waste treatment system is often subject to wide variation. Table 2 lists the variations in wastewater characteristics found by EPA in its survey of the electroplating industry. The table shows variations between plants as well as within each plant. It is essential that the variations be understood and that the waste treatment system be sized to handle variations that cannot be eliminated.

In this section, the capital and operating costs of the treatment system are discussed under five categories:

- Chromium reduction
- Cyanide oxidation
- Neutralization/precipitation
- Clarification
- Sludge handling

These units can be combined into a configuration that matches the need and capital of the individual electroplater. Flow rate is a major factor in determining equipment cost, and pollutant loading and flow rate are both significant in determining the operating cost of the system. This section concludes with an example to illustrate how total costs can be estimated for a specific facility.

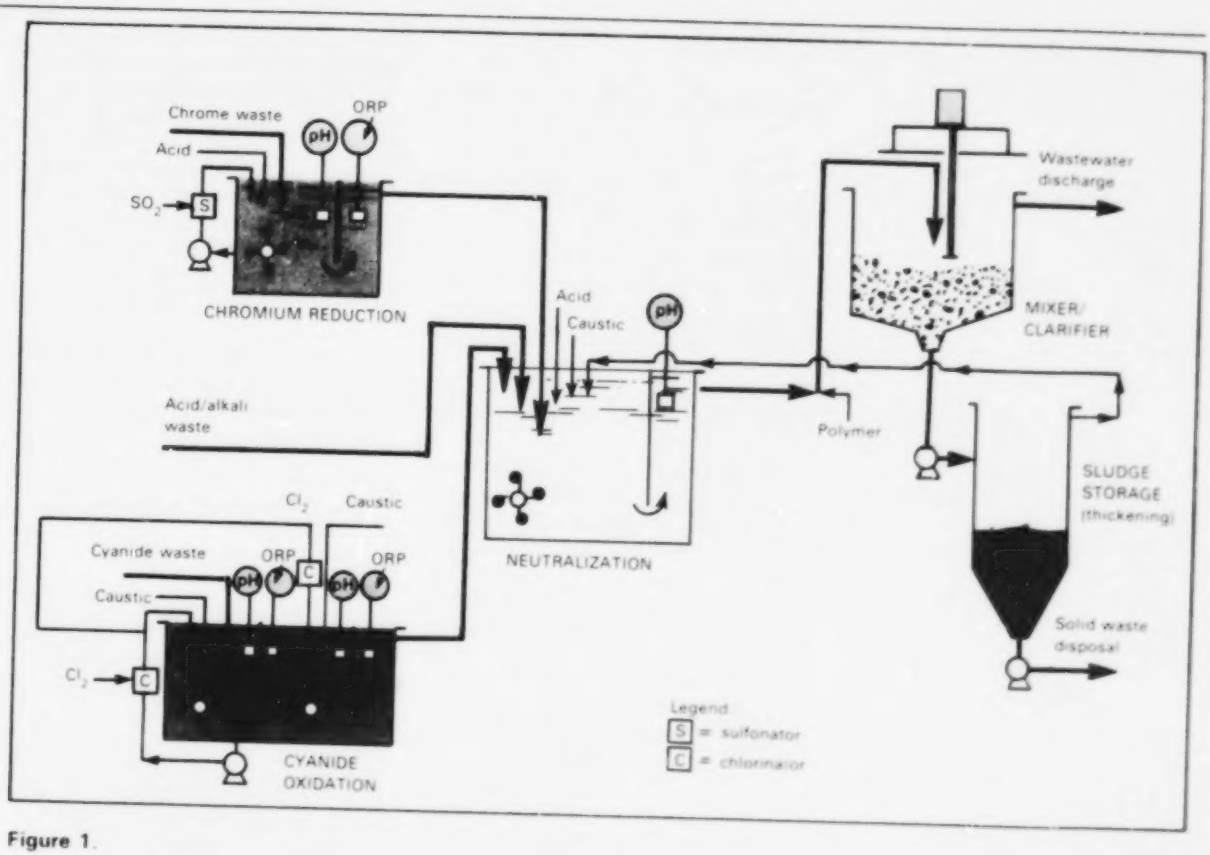


Figure 1.

Electroplating Industry Conventional Wastewater Treatment

Table 2.

Composition of Raw Waste Streams from Common Metals Plating

Constituent	Range (mg/l)
Copper	0.032-272.6
Nickel	0.019-2,964
Chromium:	
Total	0.098-635.9
Hexavalent	0.009-334.8
Zinc	0.113-282.0
Cyanide:	
Total	0.026-165.0
Amenable to chlorination	0.009-139.0
Fluoride	0.023-141.7
Cadmium	0.007-51.48
Lead	0.003-33.58
Iron	0.410-1,483
Tin	0.003-165.4
Phosphorus	0.005-144.0
Total suspended solids	0.100-6,970

SOURCE: U.S. Environmental Protection Agency, Development Document for Proposed Effluent Limits Guidelines and New Source Performance Standards for the Electroplating Point Source Category, EPA-440/1-79/003a, July 1979.

Capital Cost

General. The unit processes shown in Figure 1 are used extensively in the electroplating industry, and as a result their design has become somewhat standard. Standardization and the high cost of site preparation and construction have led to the development of skid-mounted package systems, complete with all hardware and auxiliaries. The installation costs for package systems usually will range between 10 and 30 percent of the purchase price of the equipment as compared with 70 and 150 percent for component systems.

The costs presented in the following sections assume all components of the individual systems must be purchased. Reduced costs can be realized by using existing pumps, tanks, and instrumentation. Higher installation

costs, however, can result from site-specific costs for wastewater collection systems, new building space, structural modifications, or relocation of existing equipment.

Chromium Reduction Units. Chromium complexes are usually present in electroplating wastewater as trivalent chromium (Cr^{+3}) or as hexavalent chromium (Cr^{+6}). Although most heavy metals are precipitated readily as insoluble hydroxides by pH adjustment in the neutralizer, hexavalent chromium first must be reduced to trivalent chromium. Reduction usually is done by reaction with gaseous sulfur dioxide (SO_2) or a solution of sodium bisulfite ($NaHSO_3$). The net reaction using sulfur dioxide is:

$$3SO_2 + 2H_2CrO_4 + 3H_2O \rightarrow Cr_2(SO_4)_3 + 5H_2O$$

Because the reaction proceeds rapidly at low pH, an acid is added to control the chromic acid wastewater pH between 2 and 3. Gaseous sulfur dioxide is metered continuously into the reaction tank to satisfy the reduction demand based on the concentration of hexavalent chromium.

The installation and package unit costs for continuous and batch chromium reduction systems are shown in Figure 2. The continuous system costs are for units using sulfur dioxide as the reducing agent, as shown in Figure 1. The cost includes storage and feed systems for the treatment reagents. The batch system cost is for a system with two reaction tanks, each sized to hold 4 hours of wastewater flow and equipped with high level alarms, portable pH and oxidation reduction potential (ORP) probes, a portable mixer, and storage tanks and feed pumps to add sodium metabisulfite and sulfuric acid to the reaction tanks.

For very small flows, simpler and less costly batch systems are feasible. Figure 2 includes the costs for hardware, piping, instrumentation, and utility connections. The graph shows that the initial cost of batch chromium reduction systems is more attractive for wastewater flow rates below 20 gal/min (76 l/min). The smallest continuous units are rated to process up to 30 gal/min (113 l/min) wastewater.

Cyanide Oxidation Units. Dilute cyanide rinse streams resulting from plating operations and cyanide dips also must be treated separately to oxidize the highly toxic cyanide, first to less toxic cyanate, then to harmless bicarbonates and nitrogen. The oxidation reagent is usually chlorine, which can be introduced into the system by adding chlorine gas (Cl_2) or sodium hypochlorite (NaOCl). Using chlorine, the typical reaction in the first stage is:

$$NaCN + 2NaOH + Cl_2 \rightarrow NaCNO + 2NaCl + H_2O$$

and in the second stage,

$$2NaCNO + 5NaOH + 3Cl_2 \rightarrow 6NaCl + CO_2 + N_2 + NaHCO_3 + 2H_2O$$

When sodium hypochlorite is used, the typical reaction in the first stage is:

$$NaCN + NaOCl \rightarrow NaCNO + NaCl$$

and in the second stage,

$$2NaCNO + 3NaOCl + H_2O \rightarrow 3NaCl + N_2 + 2NaHCO_3$$

Continuous systems (Figure 1) use two series-connected reaction tanks. In the first stage, the pH is adjusted

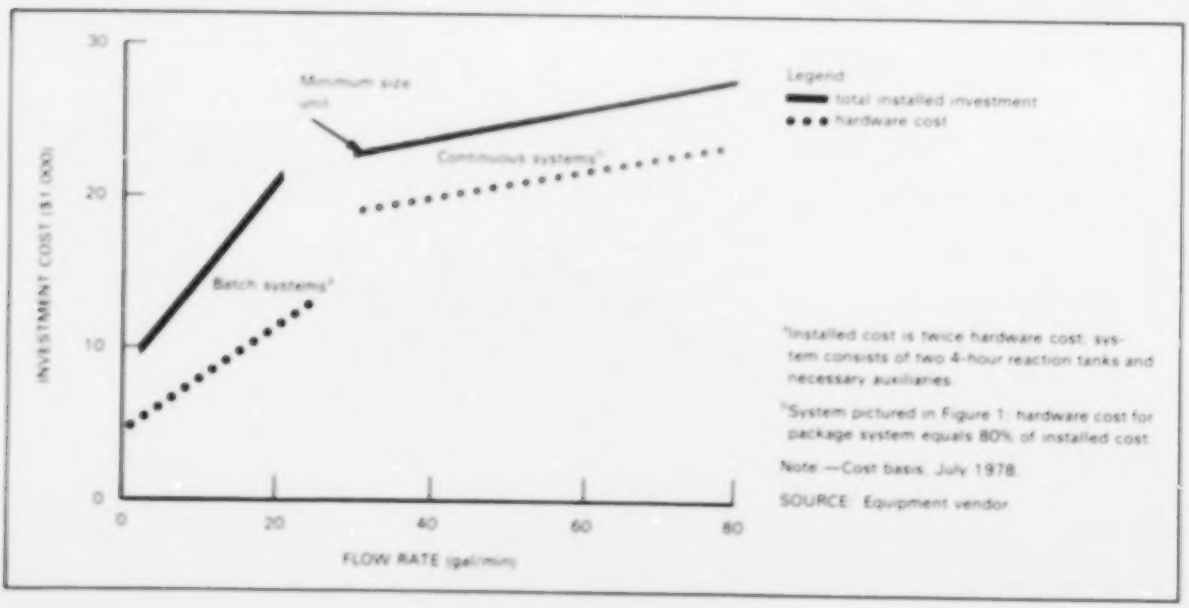
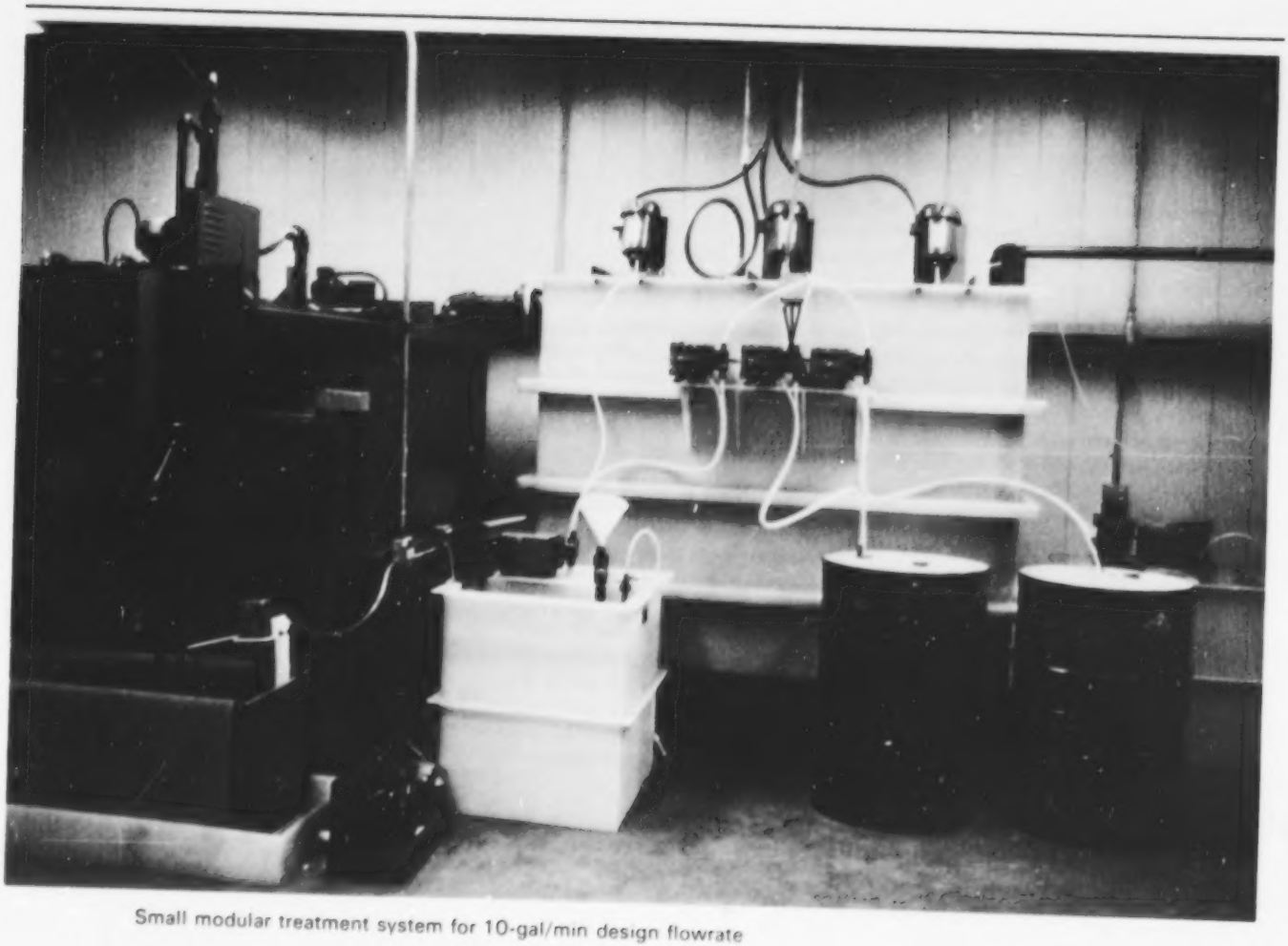


Figure 2.

Investment Cost for Chromium Reduction Units



Small modular treatment system for 10-gal/min design flowrate

between 9 and 11 using an alkali such as caustic or lime. The pH in the second reaction chamber is controlled at approximately 8.5. Chlorine is added continuously to both stages. Because the demand for chlorine in the second stage is proportional to demand in the first stage, the chlorine is fed to both stages from the same feeder at a set ratio based on demand in the first stage. Demand in the first stage is determined by measuring ORP. The reaction time needed is approximately 25 to 30 minutes in each stage.

Figure 3 presents the installed cost curves for continuous and manual batch systems. The continuous system cost is for the unit shown in Figure 1, which uses chlorine gas as the oxidizing agent. The cost includes storage and feed systems for the treatment reagents. The batch system cost is for a system with two 4-hour reaction tanks and the required auxiliaries associated with oxidizing the cyanide with sodium hypochlorite and caustic.

Again, for very small flows, simpler and less costly batch systems are feasible. At wastewater flow rates below 20 gal/min (76 l/min) batch systems should be considered. At higher flow rates, the labor cost savings make the total cost to operate a continuous system (depreciation plus operating cost) less than the total cost to operate a batch system.

Neutralization/Precipitation Techniques. The mixed acid/alkali waste streams from the various metal cleaning and plating operations are combined in the neutralizer with the effluent from the chromium reduction and cyanide oxidation steps. Because the heavy metals are soluble at low pH (acidic) conditions in the wastewater, the pH is adjusted to a range of 7.5 to 9.5. In this pH range, the minimum solubility of a mixture of metals is reached and the metals precipitate as hydroxides.

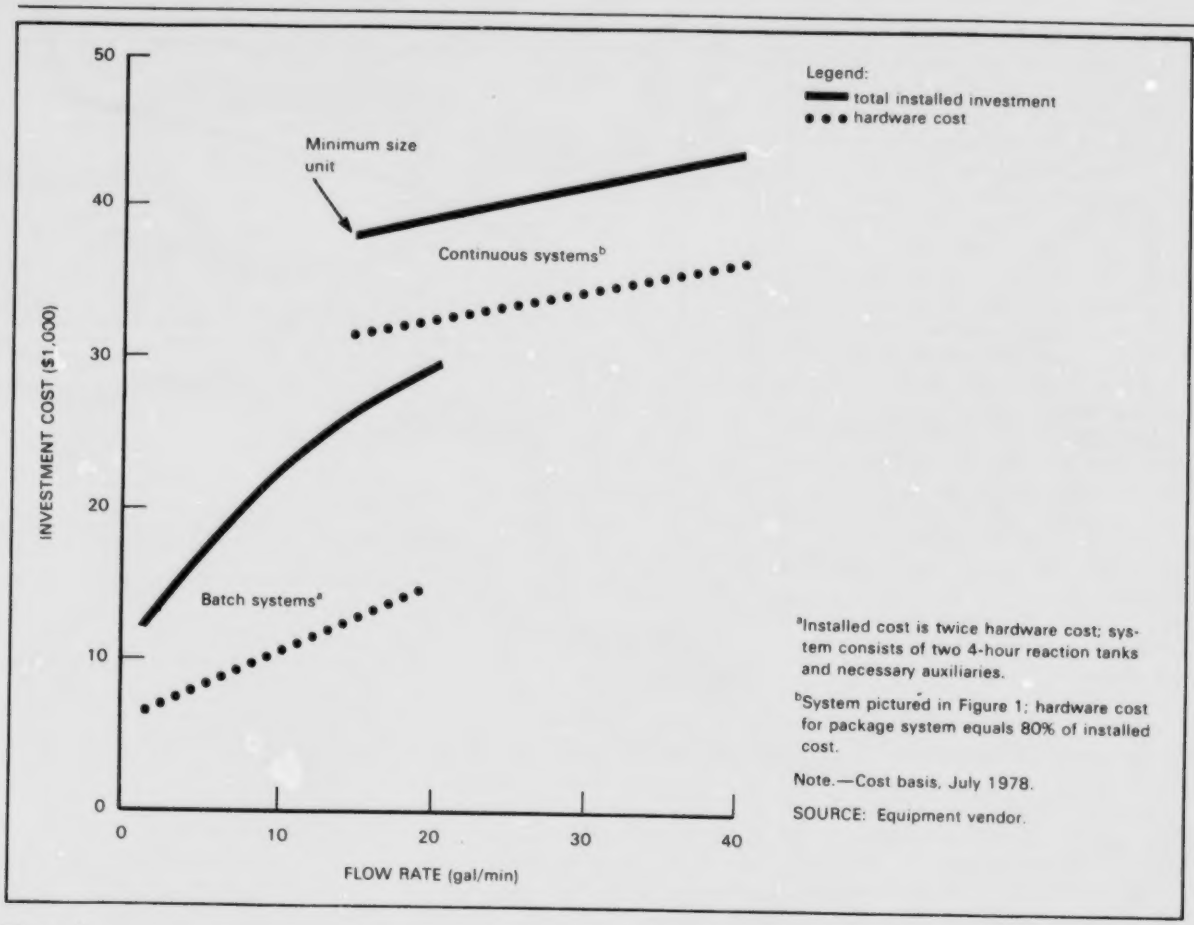


Figure 3.

Investment Cost for Cyanide Oxidation Units

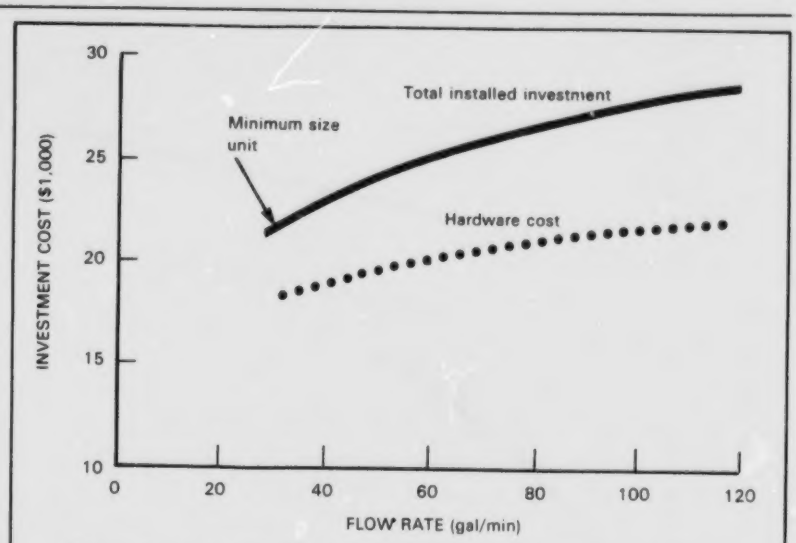
Many types of neutralization systems can be designed with various degrees of automation and controls, depending on the volumetric flow rates and the variability of the flow rates or pH entering the neutralizer. Because a change of 1 pH unit represents a tenfold change in hydrogen ion concentration (Table 3), it will be difficult to maintain the pH in the narrow range where maximum removal of pollutants is realized if the neutralizer feed is subject to wide variations.

Table 3.

Ion Concentration vs. pH for Water Solutions

pH	Free hydrogen ion (acid) concentration (gram-ions/liter)	Free hydroxyl ion (base) concentration (gram-ions/liter)
1	0.1	0.0000000000001
2	0.01	0.0000000000001
3	0.001	0.00000000001
4	0.0001	0.0000000001
5	0.00001	0.000000001
6	0.000001	0.00000001
7 (neutral)	0.0000001	0.0000001
8	0.00000001	0.000001
9	0.000000001	0.00001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.0000000000001	0.1

Single-stage, continuous neutralizers—where all the alkali such as lime, $Ca(OH)_2$, or caustic soda, NaOH, is fed into a single reaction vessel—are usually suitable for electroplating applications. If, however, the wastewater is subject to rapid changes in flow rates or pH, a multistage neutralizer is required. In the multistage units, most of the alkali is added in the first vessel to increase the pH to 6. Final pH adjustments of the wastewater are made in the remaining reaction vessels to promote precipitation and to enhance the settling characteristics of the metal hydroxides. To maintain adequate pH control, the retention time for typical neutralization systems is 10 to 30 minutes. A system using lime usually requires more retention time, as the time required for completely dissolving the lime retards the response of the system to the reagent addition.



Notes.—Cost basis, July 1978. Hardware cost for package system equals 80% of installed cost.

SOURCE: Equipment vendor.

Figure 4

Installed Cost for Continuous Single-Stage Neutralization/Precipitation System

Figure 4 shows the installed cost for a continuous neutralization system (see Figure 1) typically used in the electroplating industry. This system is single stage with pH-controlled addition of the treatment chemicals; caustic soda is used as the alkali and sulfuric acid is used as the acid.

Clarification. Metal hydroxides and other insoluble pollutants are removed from the wastewater by gravity settling. The solids removal efficiency depends on the settling rate of suspended solids in the wastewater feed. Typically, some of these solids settle very slowly because of their small size and their slight density difference compared with the water. Because economical design of the clarifier limits the retention time in the settling chamber, some level of suspended solids will appear in the overflow.

To enhance the settling characteristics of the suspended solids, flocculating agents—such as polymers, alum, or ferrous sulfate—are added in a mixing chamber before the flocculator. In the flocculator, the wastewater is agitated gently to allow the solids to coagulate. The wastewater then enters the clarifier, where the solids settle out. The solids in the underflow can be discharged to a holding tank for thickening, or they can be discharged directly to sludge disposal. The optimum dosages of flocculating agents, the size and costs for flocculation and clarification hardware, and the associated solids removal efficiencies can be estimated only by laboratory testing.

Figure 5 shows hardware and total installed costs for flocculation and clarification systems typically employed in the electroplating industry. These costs are presented as a function of volumetric flow rate, but they will depend also on the solids settling rates and the level of solids allowed in the effluent.

Sludge Handling. The solids from clarifiers are typically discharged to sludge holding tanks at solids concentrations of 0.5 to 3 percent; overflow from the tank is recycled to the clarifier. Usually metal hydroxide solids will concentrate to approximately 3- to 5-percent solids in these tanks if given adequate retention time. The tanks also provide adequate storage time and volume for the sludge before shipment to a disposal site.

Figure 6 shows the investment for tanks used for sludge storage as a function of tank volume.

Further concentration of the thickened sludge requires the use of mechanical dewatering equipment. Centrifuges, rotary vacuum filters, belt filters, and filter presses have been used to dewater metal hydroxide sludge. The applicability of a particular dewatering device for a specific sludge, and the degree of cake dryness the device will achieve, can only be determined by bench-scale testing with the intended feed material.

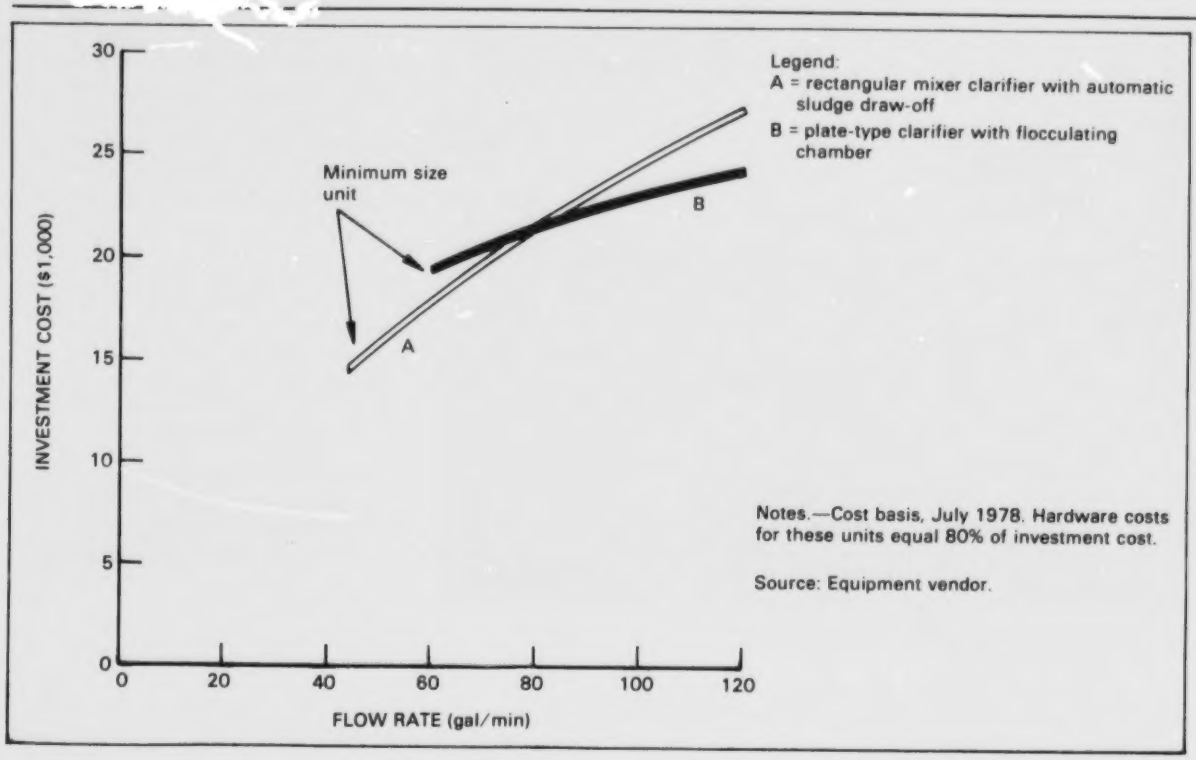


Figure 5.

Installed Cost for Flocculation/Clarification System

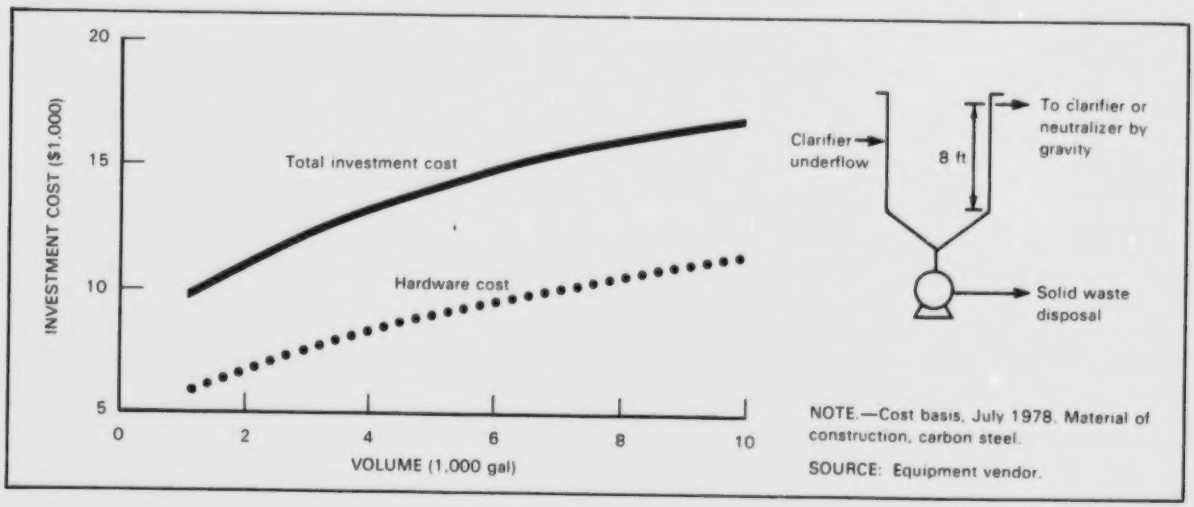
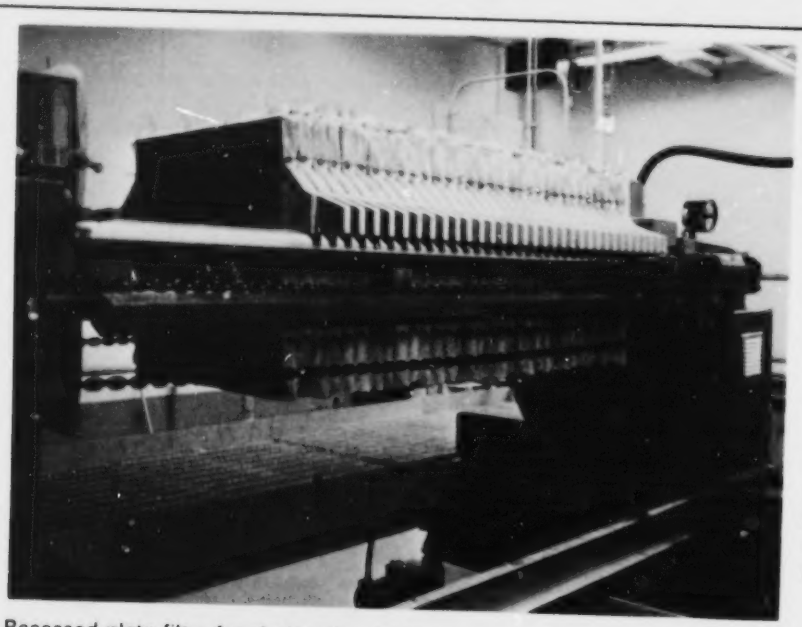


Figure 6.

Installed Cost for Sludge Storage/Thickening Tank



Recessed plate filter for sludge dewatering

Figure 7 presents the unit costs for recessed plate filter presses as a function of the filter cake volume of the unit. The feed volume capacity of the unit is also given, based on an assumed feed and cake solids concentration and a press cycle time of 4 hours.

The costs shown in Figure 7 do not include costs of installation or of the auxiliary equipment associated with the press, because these costs are both variable and site specific. Items that will contribute to the total cost of the installation include:

- High pressure feed pump(s)
- Sludge feed storage
- Filtrate return to clarifier
- Cake solids handling and discharge

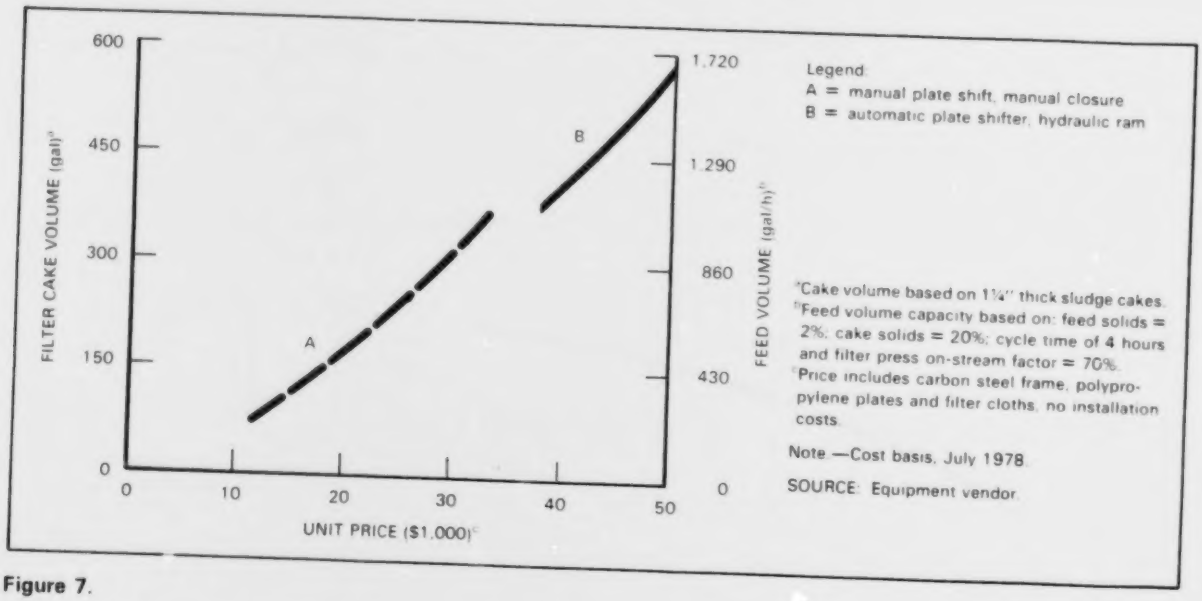


Figure 7.

Unit Prices for Recessed Plate Filter Presses

Operating Costs

Basis. Although the investment costs for conventional wastewater treatment systems depend principally on wastewater flow rate, the operating costs will depend on the following factors:

- Utility costs (primarily electricity to operate pumps and agitators)
- Overhead and depreciation
- Sludge disposal costs and municipal sewer charges (sludge disposal cost dependent on contract hauling distances and disposal requirements, municipal sewer fees based on volumetric discharge)
- Chemicals (costs based on pollutant loading and types of treatment chemicals)
- Operating and maintenance labor

The chemical and sludge disposal costs offer the best opportunity for cost savings because labor and utility requirements are usually fixed, based on the design and operational procedures. Table 4 shows the basis for estimating economics used in this report.

Sludge Disposal and Municipal Charges. Installation of wastewater treatment systems will result in the discharge of two streams: overflow from the clarifier and sludge from the clarifier or thickener/holding tank. The costs associated with these discharges will be site specific for each plant, and will depend on the availability of local disposal sites to receive the sludge and on municipal sewer costs. All these costs probably will escalate as the regulations are implemented.

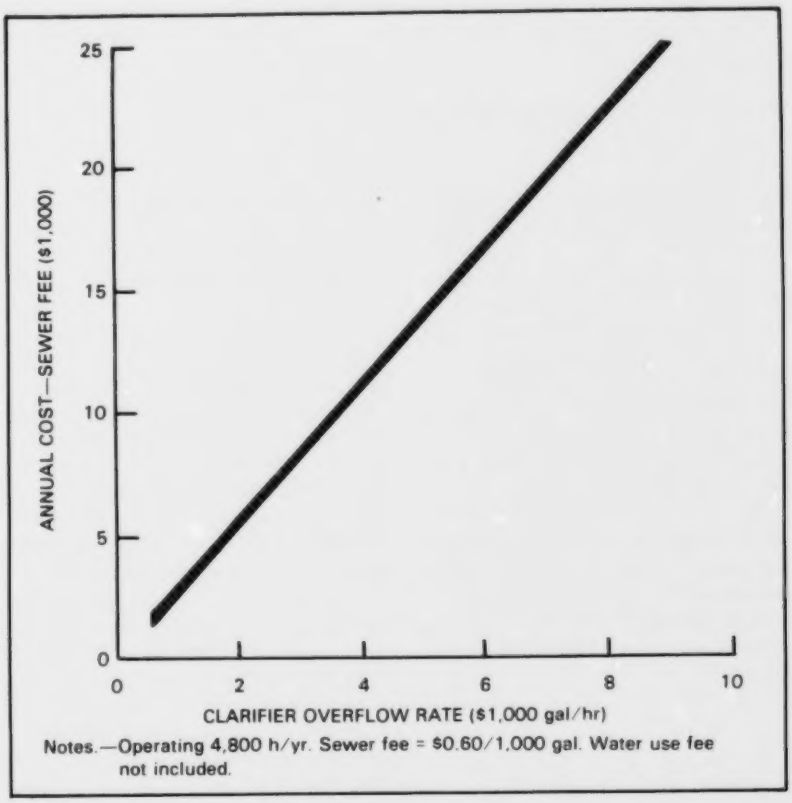
Typical charges for sewer fees for a major city were presented in Table 1. Figure 8 shows the effects of wastewater flow rates on sewer fees, based on a sewer fee of $0.60/1,000 gal.

Table 4.

Basis for Economic Evaluations

Item	Basis
Annual operating costs:	
Operating labor	$7/h
Supervision	$9/h
Maintenance	6% of investment
General plant overhead	0.58 (operating + supervisory + maintenance labor); maintenance labor = 0.37 (maintenance cost)
Depreciation (10-year straight line)	10% of investment
Taxes and insurance	1% of investment
Utility charges:	
Electricity	$0.045/kWh
Cooling water (cooling tower)	$0.10/1,000 gal
Steam	$3.00/1,000 lb
Net operating savings ($/yr)	Operating cost reduction resulting from investment minus increase in fixed and operating cost for new system
Net saving after taxes ($/yr)	Net operating savings × 0.52 (assumes 48% tax rate)
Return on investment	Net savings after taxes ÷ total installed investment
Cash flow ($/yr)	Net savings after taxes + depreciation
Payback period (yr)	Total installed investment ÷ cash flow

Note.—No interest on capital is included in the economic analyses.



Notes.—Operating 4,800 h/yr. Sewer fee = $0.60/1,000 gal. Water use fee not included.

Figure 8.

Annual Sewer Fee as a Function of Clarifier Overflow Rate

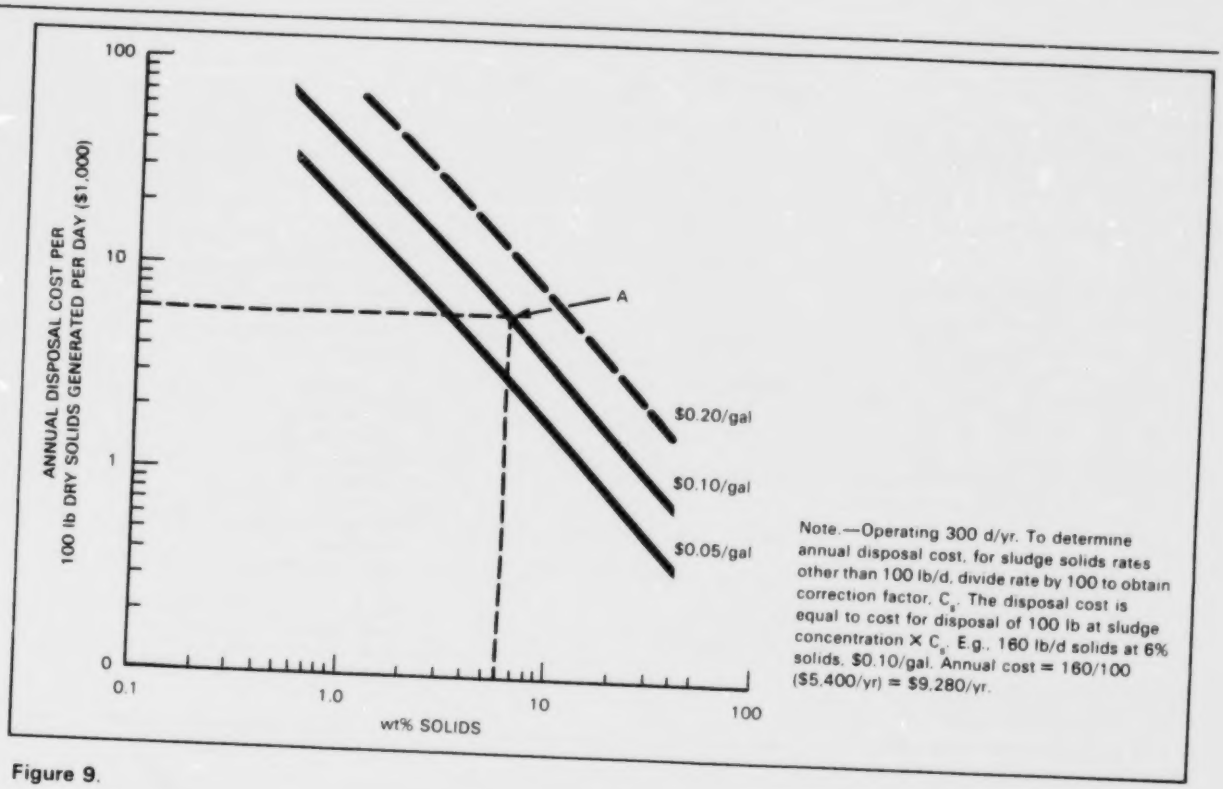

ANNUAL DISPOSAL COST PER
100 lb DRY SOLIDS GENERATED PER DAY ($1,000)
100
10
1
0
0.1
1.0
10
100
wt% SOLIDS
A
$0.20/gal
$0.10/gal
$0.05/gal
Note.—Operating 300 d/yr. To determine annual disposal cost, for sludge solids rates other than 100 lb/d, divide rate by 100 to obtain correction factor, C_s. The disposal cost is equal to cost for disposal of 100 lb at sludge concentration × C_s. E.g., 160 lb/d solids at 6% solids, $0.10/gal. Annual cost = 160/100 ($5,400/yr) = $9,280/yr.

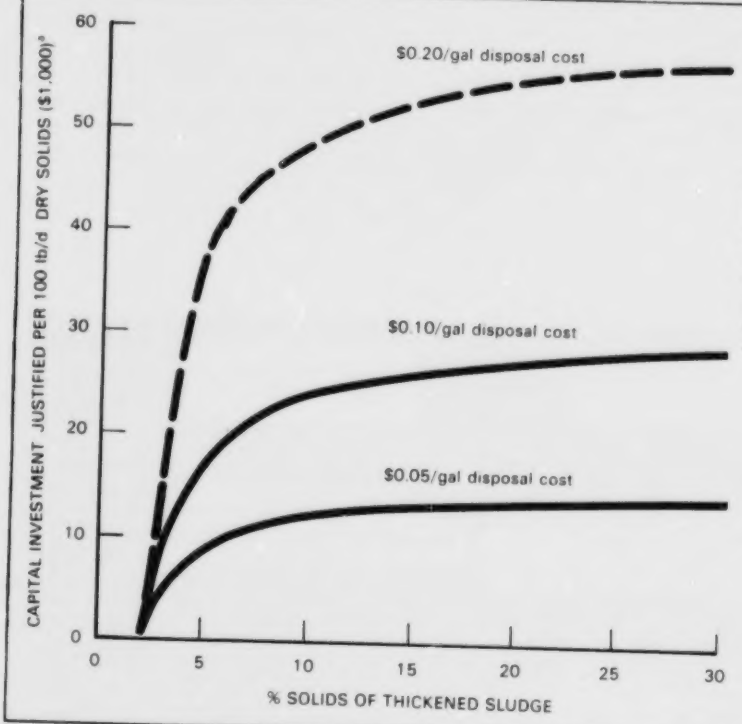
Figure 9.

Annual Cost for Disposal of Industrial Sludge

Assuming the sludge will be hauled to a licensed chemical landfill, the costs will depend on the volume of sludge, the distance hauled, and the sludge composition. In most areas, the costs of sludge disposal are currently in the range of $0.05/gal to $0.20/gal, but there are cases where disposal costs run as high as $0.50/gal. Figure 9 shows the annual costs for disposal of each 100 pounds (45 kg) of solids over a range of sludge concentrations and disposal costs. If 100 pounds (45 kg) of solids are present in the sludge at a concentration of 6 percent, the annual cost for disposal is $6,000 at a disposal cost of $0.10/gal (point A on Figure 9).

The disposal cost savings achievable by thickening also can be estimated by using Figure 9 to calculate the difference between the disposal costs at the present concentration and the projected final concentration after thickening. For example, a plant now disposes of 200 lb/d (90.7 kg/d) of dry solids as a sludge with a concentration of 1 percent solids. At $0.10/gal of sludge, the disposal cost would be $72,000 per year ($36,000 × 200/100 pounds dry solids). A test on the performance of a thickening tank predicted a further thickening to 2 percent solids. At this concentration, the sludge disposal costs would decrease to $36,000 ($18,000 × 200/100 pounds dry solids). The disposal cost savings for thickening the sludge from 1 percent to 2 percent would be $36,000 ($72,000 – $36,000).

Further dewatering of metal hydroxide sludges by mechanical dewatering equipment can reach solids concentrations in the range of 15 to 50 percent. Figure 10 shows the total installed investment that could be justified for additional dewatering equipment to concentrate a sludge containing 2 percent solids to higher solids concentrations. The cost reduction used to calculate this return on investment (ROI) did not take into account variable operating costs, such as utility costs and operating labor, which for mechanical dewatering devices could be significant. These additional costs would result in a lower ROI.



Dewatering Equipment Performance

Type	Approximate cake solids (%)	Approximate maximum feed rate (gal/min)
Thickener	3-10	3,000
Basket centrifuge	10-30	100
Decanter centrifuge	10-30	250
Drum vacuum filter	10-35	250
Vacuum belt filter	10-20	50
Pressure filter	15-45	250
Gravity/pressure belt	10-35	200

[a]At 40% ROI (pretax). ROI = (disposal cost savings[b] − fixed cost[c]) ÷ capital investment.

[b]300 operating d/yr, from Figure 9.

[c]Includes depreciation, taxes, insurance, and maintenance. Utility and labor costs not included.

Note.—Initial solids concentration of 2% (clarifier underflow). Solids concentration vs gallons sludge: 2% = 600 gal/100 lb solids; 5% = 232 gal/100 lb solids; 10% = 112 gal/100 lb solids; 30% = 32 gal/100 lb solids.

Figure 10.

Investment Justified for Sludge Thickening Equipment

Because the volume of sludge does not change radically at concentrations above 10 percent, there is a decrease in economic incentive to invest in additional dewatering equipment to provide concentrations above this level, as is indicated by the decreasing slope of the curve in Figure 10. For this particular case, the plant would not generate significant additional savings by selecting a system that concentrated the solids beyond 8 to 12 percent.

To illustrate the disposal cost savings that can be realized by mechanical dewatering of a dilute sludge, assume that the same plant was able to concentrate the thickener tank bottoms from 2 to 20 percent solids with a filter press. The annual disposal cost would be reduced from $36,000 to $3,200 (Figure 9, $1,600 × 200/100). The capital investment justified to achieve this saving, using the basis developed in Figure 10, is $54,000 ($27,000 × 200/100). Figure 7 defines the cost of filter presses as a function of cake volume and feed-processing capacity. Using the feed-processing capacity, the press feed rate would equal:

$$\frac{200 \text{ lb solids}}{\text{d}} \div \frac{0.02 \text{ lb solids}}{\text{lb}} \times \frac{\text{gal sludge}}{8.34 \text{ lb/gal}} = \frac{1{,}200 \text{ gal sludge}}{\text{d}} \times \frac{\text{d}}{8\text{h}} = \frac{150 \text{ gal sludge}}{\text{h}}$$

From Figure 7, the minimum size commercial unit could dewater this feed rate and would cost $11,500. Assuming the total installed cost of the system is twice the press cost, or $23,000, the ROI would be well in excess of the 40 percent used as a basis for Figure 10.

Chemical Costs. The concentration of pollutants, the volumetric flow rate of the waste stream, and the types of chemicals chosen for wastewater treatment will affect the chemical costs. The demand for treatment chemicals will be proportional to the volumetric flow of the wastewater if the composition of the wastewater is constant. Because the addition of chemicals involves a chemical reaction with the pollutants, the types of treatment chemicals selected will produce different use rates, volumes of sludge for disposal, and removal efficiencies. All these factors affect the operating costs and must be considered by the plant.

Common treatment reagents used in the electroplating industry are SO_2 for chromium reduction, chlorine for cyanide oxidation, and caustic soda for neutralization/precipitation. These chemicals, and the chemical costs given in Table 1, were used to provide the cost model for the conventional wastewater treatment systems shown in Figure 11. This figure enables the user to calculate the consumption of treatment chemicals (consumption factor) and the associated cost (cost factor), based on the mass flow of each pollutant and the volumetric flow rate of the wastewater being treated. The sludge disposal cost model (shown in Figure 12) can be used to determine the dry solids generated by precipitation of the heavy metals contained in the waste stream. Figure 12 also defines the cost for disposal of each pound of metal precipitated, assuming the resulting sludge is disposed of at 4 percent solids concentration at a cost of $0.10/gal.

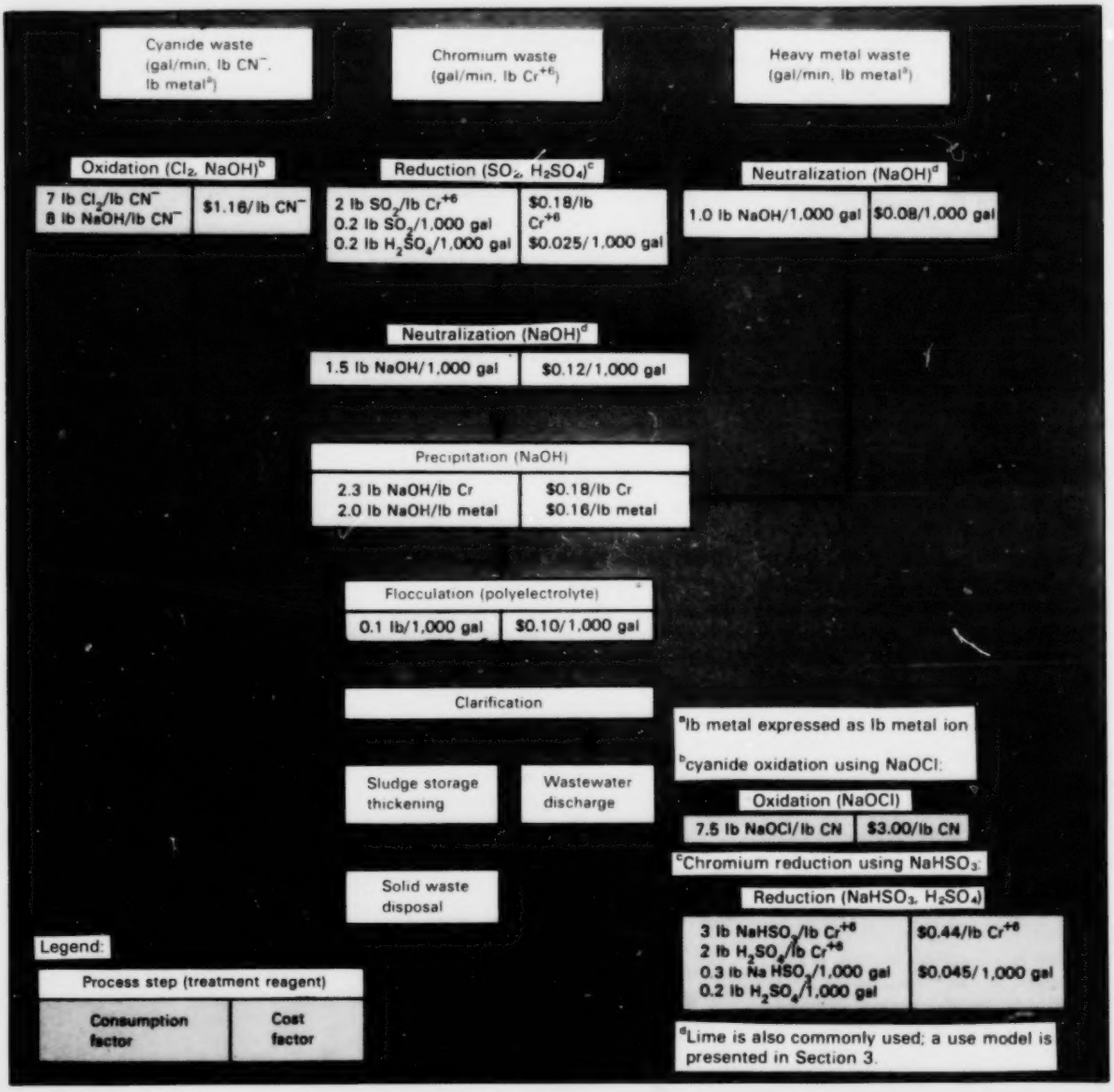


Figure 11.

Consumption and Cost Factors for Wastewater Treatment Chemicals

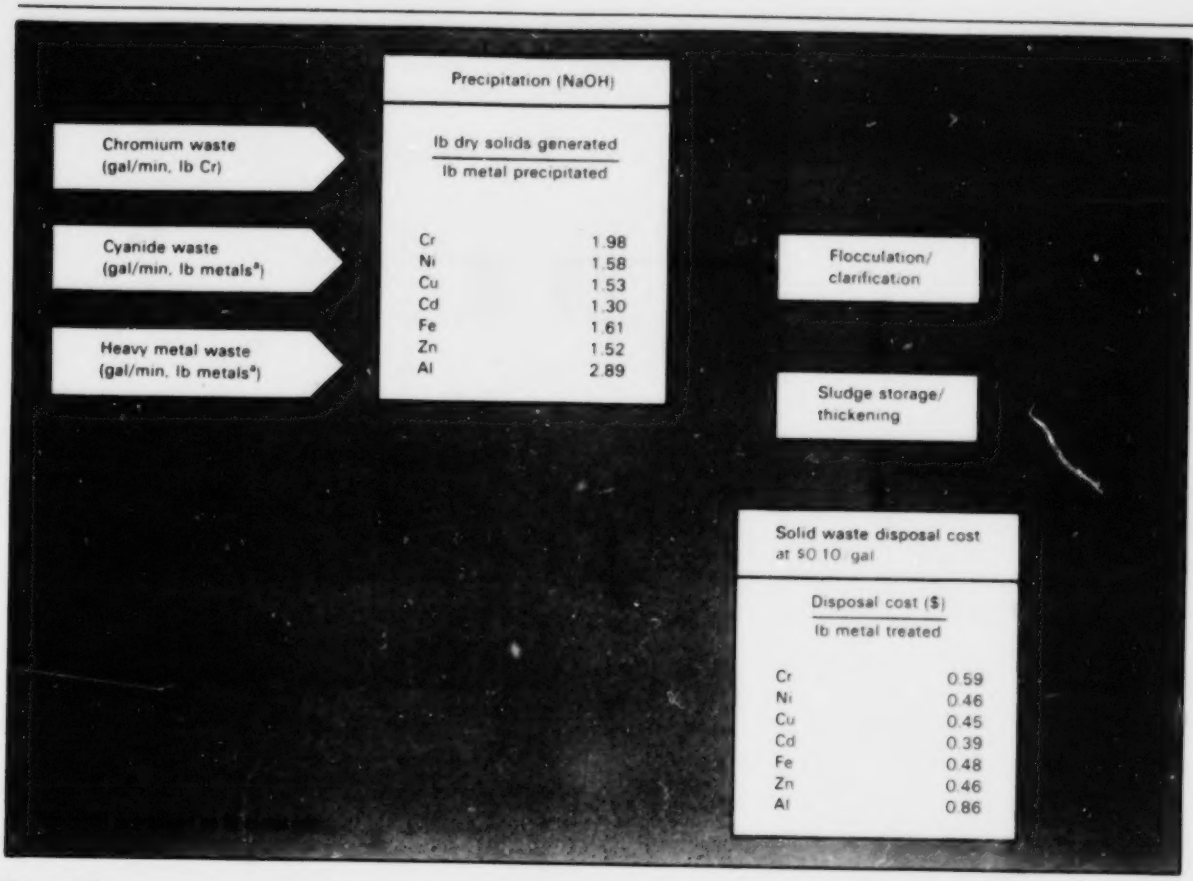


Figure 12.

Sludge Disposal, Solids Generation, and Disposal Cost Model

The cost models in Figures 11 and 12 can be used together to determine the incremental costs associated with removing each pound of pollutant and treating each gallon of wastewater entering the system. These models will be used to predict the impact of water use reduction programs, chemical recycle systems, and other modifications on the cost of operating a wastewater treatment system.

Determining the Total Annual Cost of Wastewater Treatment

The information presented in this section makes it possible to determine both the investment required and the operating cost of a conventional wastewater treatment system for an electroplating facility. As an example, Figure 13 illustrates the wastewater characteristics and the required treatment steps needed to remove the pollutants from the wastewater before discharge. The plant had chromium, cyanide, and a mixed acid/heavy metals wastewater entering the treatment system.

Table 5 presents the chemical treatment and sludge disposal costs using the factors presented in Figures 11 and 12. Based on 4,800 h/yr operation (16 h/d, 300 d/yr), costs are $17,500/yr for chemical treatment and $19,300/yr for sludge disposal. The required investment for treatment hardware is calculated in Table 6, using the equipment cost data presented in this section. Table 7 converts this cost into an annual cost using the basis defined in Table 4, and includes projected manpower requirements and utility consumption to give a total annual cost of $100,000.

A similar analysis can be made by any plant once the wastewater flow rates and characteristics are known.

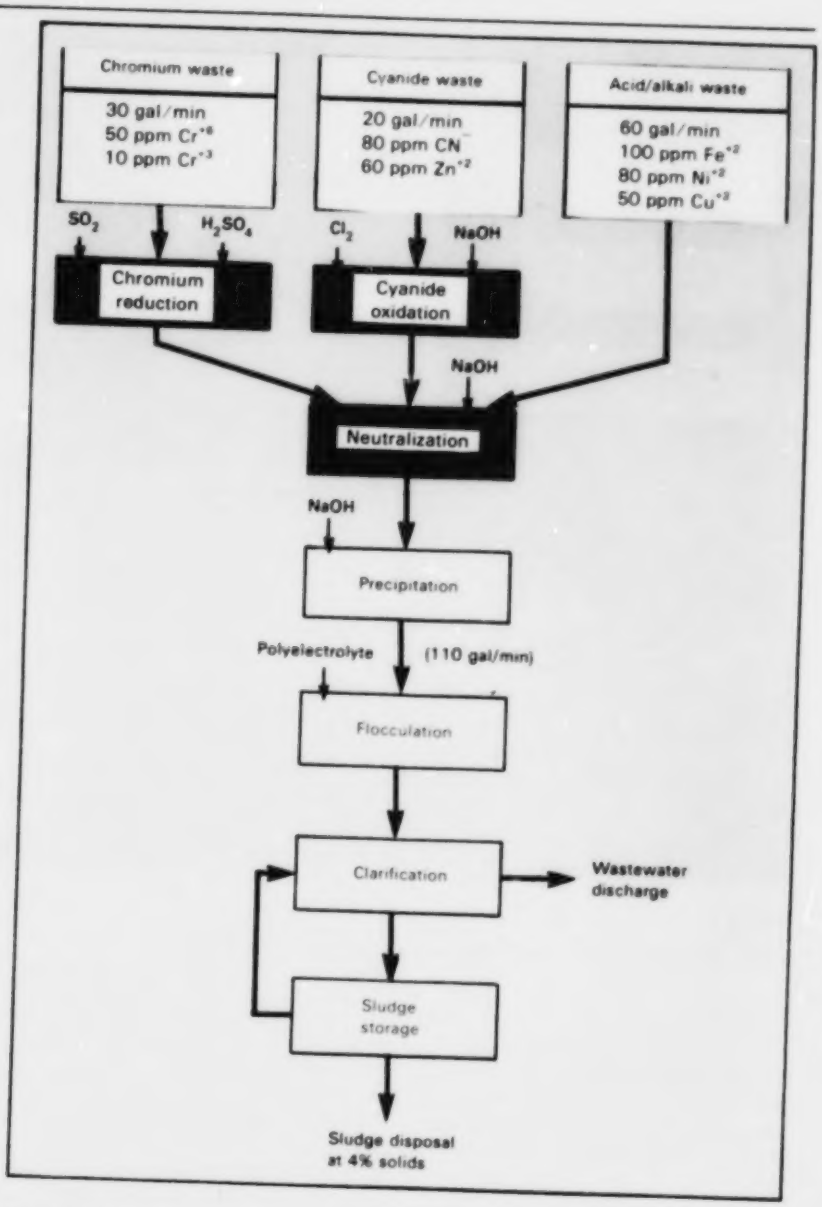


Figure 13.

Electroplating Wastewater Treatment Flow Chart: Example System

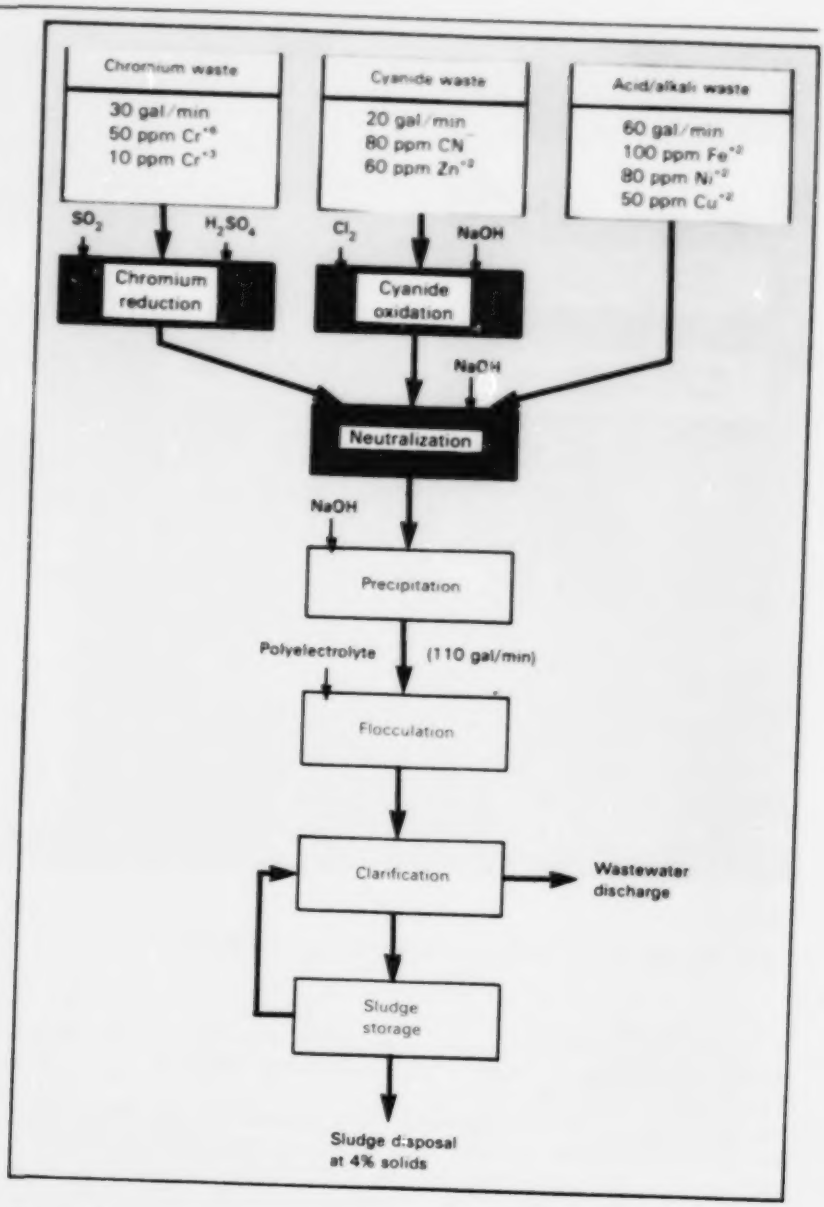


Figure 13.

Electroplating Wastewater Treatment Flow Chart: Example System

Table 5.

Chemical and Sludge Disposal Cost: Example System[a]

Treatment step	Waste streams	Treatment chemicals		Sludge disposal		Total annual costs ($)
		Rates (lb/h)	Cost rates ($/h)	Dry solids generated (lb/h)	Disposal cost ($/h)	
Chromium reduction	30 gal/min = 1,800 gal/h 0.75 lb/h Cr^{+6} 0.15 lb/h Cr^{+3}	1.86 SO_2 0.36 H_2SO_4	0.18			
Cyanide oxidation	20 gal/min = 1,200 gal/h 0.80 lb/h CN^- 0.60 lb/h Zn^{+2}	5.6 Cl_2 6.4 NaOH	0.93			
Neutralization:						
Chrome effluent	1,800 gal/h	2.7 NaOH	0.22			
Cyanide effluent	1,200 gal/h	[b]	[b]			
Acid/alkali waste	60 gal/min = 3,600 gal/h	3.6 NaOH	0.29			
Precipitation	0.90 lb/h Cr^{+3}	2.1 NaOH	0.17	1.80	0.53	
	0.60 lb/h Zn^{+2}	1.2 NaOH	0.10	0.91	0.28	
	3.01 lb/h Fe^{+2}	6.0 NaOH	0.48	4.83	1.44	
	2.41 lb/h Ni^{+2}	4.8 NaOH	0.38	3.80	1.10	
	1.51 lb/h Cu^{+2}	3.0 NaOH	0.24	2.30	0.68	
Subtotal, precipitation		17.1 NaOH	1.37	13.64	4.03	
Flocculation	110 gal/min = 6,600 gal/h	0.66 polyelectrolyte	0.66			
Total		1.8 SO_2 0.36 H_2SO_4 5.6 Cl_2 29.8 NaOH 0.66 polyelectrolyte	3.65	13.64[c]	4.03	
Chemicals						17,500
Sludge disposal						19,300

[a]System shown in Figure 13.

[b]pH adjustment not required.

[c]Sludge volume at 4% solids = 40 gal/h.

Table 6.

Investment Cost: Example System[a]

Component	Cost ($)
Chromium reduction unit (continuous system rated at 30 gal/min, from Figure 2)	23,000
Cyanide oxidation unit (continuous system rated at 20 gal/min, from Figure 3)	40,000
Neutralizer (single-stage continuous system rated at 110 gal/min, from Figure 4)	28,000
Flocculation/clarification unit (continuous system rated at 110 gal/min, from Figure 5)	26,000
Polymer feed tank, mixer, and feed pump	3,000
Sludge storage tank (5,000-gal tank to provide sludge storage volume, from Figure 6)	13,000
Total equipment and installation cost	133,000
Contingency (10% of total equipment and installation cost)	13,000
Total installed cost	146,000

[a]System shown in Figure 13.

Table 7.

Annual Cost Summary:[a] Example System[b]

Component	Cost ($/yr)
Operating labor (based on 2 h per shift)	8,400
Supervision	(c)
Maintenance	8,800
General plant overhead	6,800
Depreciation	14,600
Taxes and insurances	1,500
Chemical cost (Table 5)	17,500
Sludge disposal cost (Table 5)	19,300
Sewer fee (Figure 8)	19,000
Utilities (electricity) (approximately 25 hp required)	4,100
Total annual cost	100,000

[a]Based on Table 4.

[b]System shown in Figure 13.

[c]None required.

3. Alternatives to Conventional Wastewater Treatment

Introduction

In many cases, proper consideration of the options available for design or operation of the conventional wastewater treatment system can lead to chemical, sludge-handling, and investment cost savings. There are some alternatives to consider before selecting a wastewater treatment system. These alternatives can also provide a cost reduction in an existing system. They are:

- Electrochemical chromium reduction
- Selection of neutralization/ precipitation chemicals
- Sulfide precipitation
- Integrated treatment for waste streams requiring individual treatment

Electrochemical Chromium Reduction

Electrochemical reduction units (Figure 14) are being marketed to compete with chromium reduction systems that use chemical reducing compounds. The process uses consumable iron electrodes and an electrical current to generate ferrous ions that react with hexavalent chromium to produce trivalent chromium as follows:

$$3Fe^{+2} + CrO_4^{-2} + 4H_2O \rightarrow 3Fe^{+3} + Cr^{+3} + 8OH^-$$

The reaction occurs rapidly and requires minimum retention time. Hexavalent chromium in the effluent can be reduced to less than 0.05 ppm. Because hydroxide ions are generated, the pH of the stream usually increases from 0.5 to 1 pH unit. If the pH of the chromium wastewater is maintained between 6 and 9, the ferric and trivalent chromium ions will precipitate as hydroxides, and the effluent can be fed directly to the clarifier, bypassing the neutralizer. At lower pH values, the chromium wastewater is fed to the neutralizer. Because ferrous ions are introduced into the wastewater, some additional solids will be generated.

Maintenance requirements include replacing electrodes biweekly and washing the electrode surfaces for 10 to 15 minutes daily with a dilute acid solution to remove any surface fouling that would reduce the electrochemical efficiency of the unit.

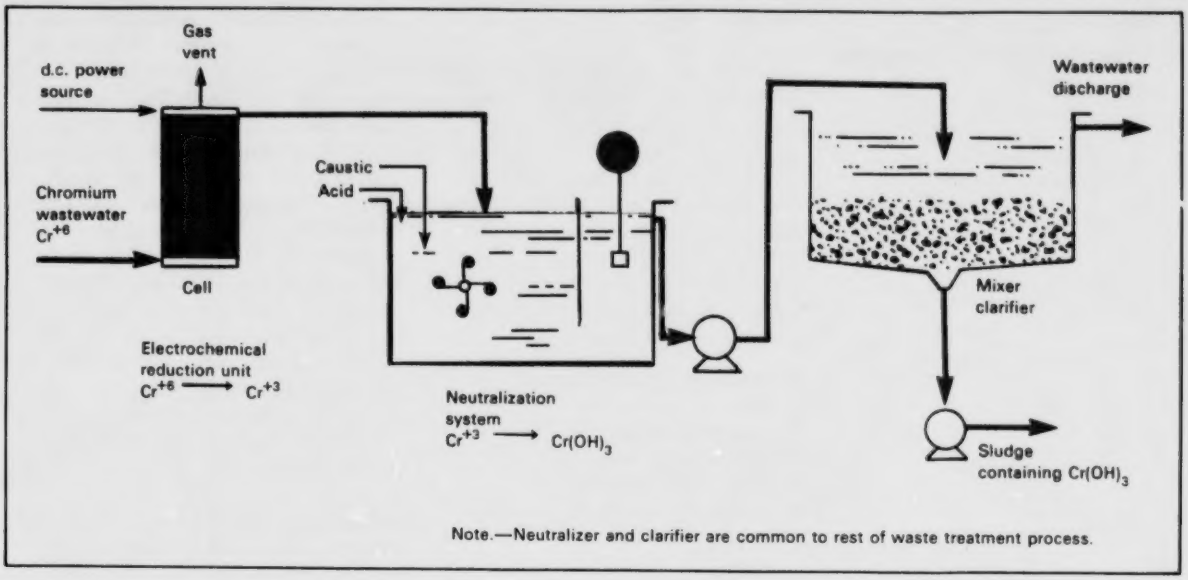


Figure 14.

Electrochemical Chromium Reduction

The investment cost and size of an electrochemical reduction system is a function of the mass flow rate[a] of the hexavalent chromium entering the unit. Figure 15 compares the installed costs for electrochemical and chemical reduction systems. Given a volumetric flow rate of 40 gal/min (151 l/min) and a hexavalent chromium concentration of 20 ppm, the total installed cost for the electrochemical unit is $36,000 or $12,000 higher than for a chemical reduction system.

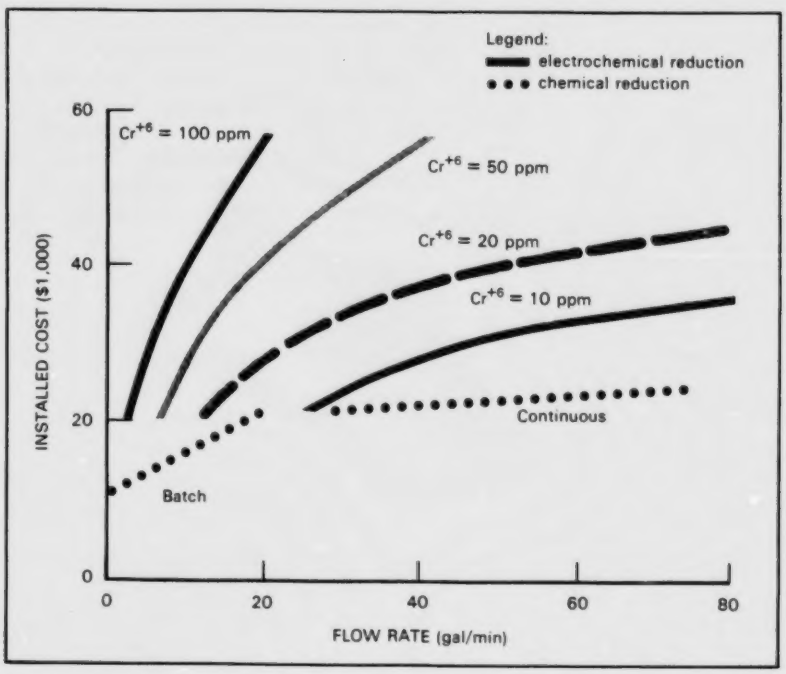


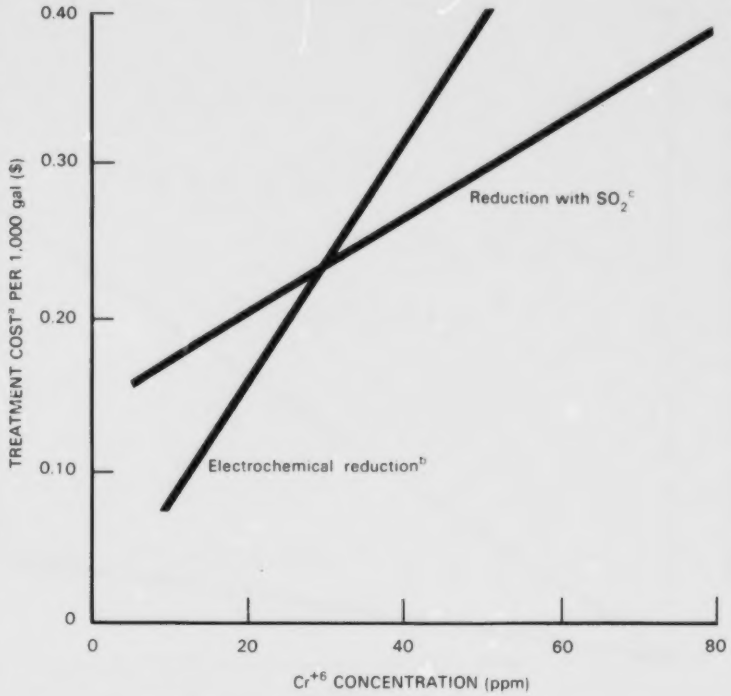
Figure 15.

Installation Cost Comparison of Electrochemical and Chemical Chromium Reduction Units

[a]Mass flow rate (lb/h) = [concentration of hexavalent chromium (ppm)] × [volumetric flow rate (gal/min)] × (0.0005, conversion factor).

Figure 16 compares the chemical and operating costs for electrochemical reduction systems and for chromium reduction using sulfur dioxide for each 1,000 gallons (3,780 liters) of wastewater being treated. These costs do not include the charge to dispose of the solids generated. The electrochemical reduction process has a treatment cost advantage until the concentration of hexavalent chromium exceeds 25 ppm. The costs of the electrochemical reduction system to treat each 10 ppm of Cr^{+6} contained in 1,000 gallons (3,780 liters) of wastewater are based on $0.07 for replacement electrodes and $0.02 for electricity (using an electricity cost of $0.045/kWh).

The major disadvantage of the electrochemical reduction system is that it results in an increased quantity of sludge; the additional sludge results from the precipitated iron hydroxide (Figure 17). Based on the sludge disposal cost model presented in Figure 12, the chemical reduction system has a combined treatment and sludge disposal cost advantage over the electrochemical system when the influent Cr^{+6} concentrations exceed 5 ppm.



[a]Excludes pumping and sludge disposal costs.
[b]Based on $0.07 for replacement electrodes and $0.02 for electricity for each 10 ppm treated.
[c]From Figure 11.

Figure 16.

Treatment Cost Comparison of Electrochemical and Chemical Chromium Reduction Units

For example, the cost to treat 1,000 gallons (3,780 liters) of wastewater containing 10 ppm of Cr^{+6} is $0.09 using an electrochemical reduction system (Figure 16). The treatment cost for a chemical reduction system would be in the range of $0.18/1,000 gal. Based on data presented in Figure 17, the chemical treatment will generate only 0.5 gallon (1.9 liter) of sludge at 4 percent solids per 1,000 gallons (3,780 liters) of wastewater treated, and the sludge disposal cost is $0.05. The electrochemical unit would generate 2 gallons (7.6 liters) of sludge at the same concentration for a disposal cost of $0.20/1,000 gal of wastewater being treated. The cost for disposal of the additional sludge would amount to $0.15/1,000 gal of water containing 10 ppm Cr^{+6} treated. The total cost (treatment plus waste disposal) would amount to $0.23/1,000 gal for chemical reduction, compared with $0.28/1,000 gal for the electrochemical system.

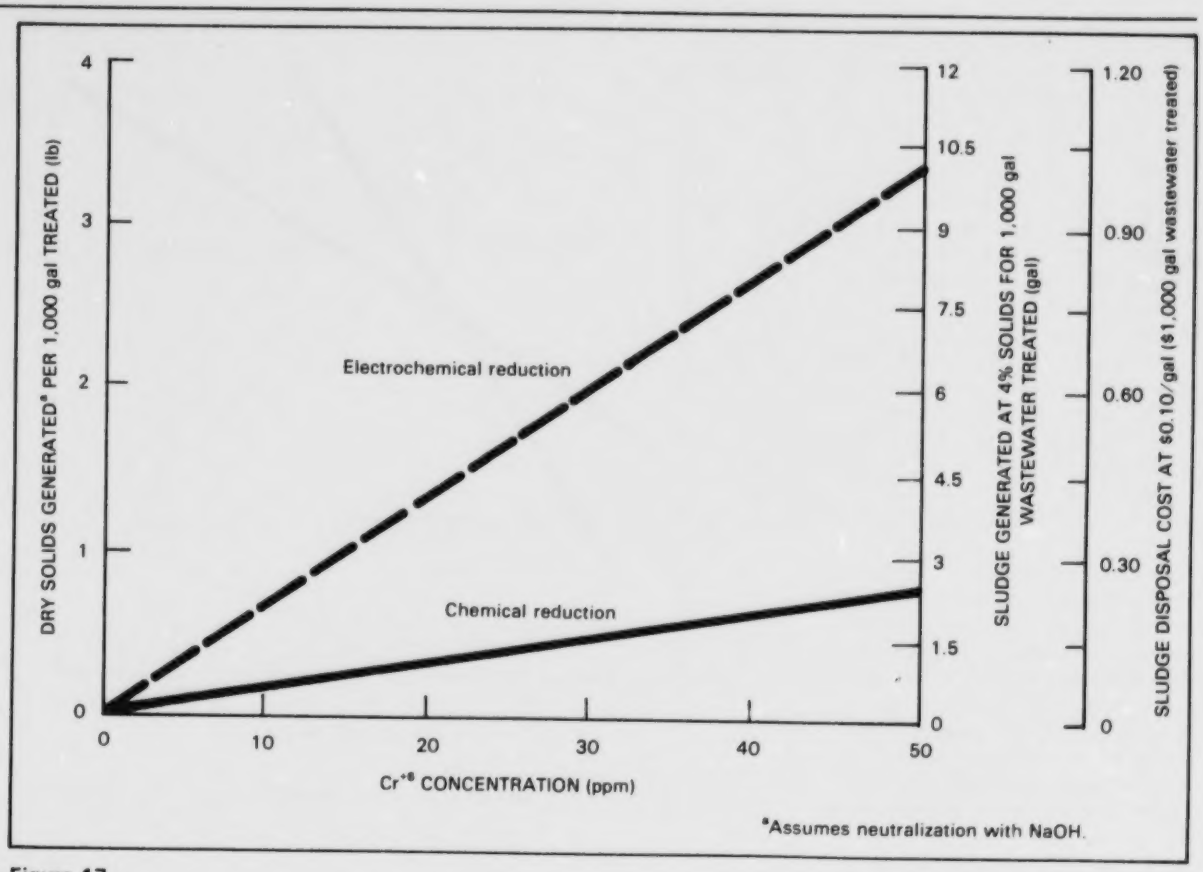

DRY SOLIDS GENERATED* PER 1,000 gal TREATED (lb)
SLUDGE GENERATED AT 4% SOLIDS FOR 1,000 gal WASTEWATER TREATED (gal)
SLUDGE DISPOSAL COST AT $0.10/gal ($1,000 gal wastewater treated)
Electrochemical reduction
Chemical reduction
Cr+6 CONCENTRATION (ppm)
*Assumes neutralization with NaOH.

Figure 17.

Sludge Generation Factors: Electrochemical vs. Chemical Chrome Reduction

Selection of Neutralization/ Precipitation Chemicals

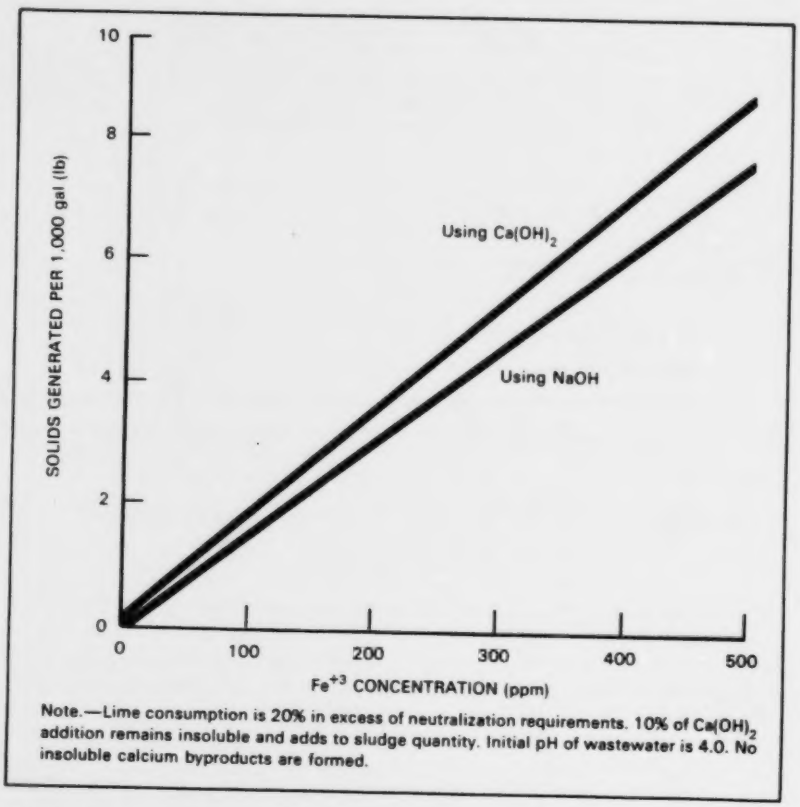
The selection of neutralization chemicals usually is based on convenience and cost factors. It must be remembered that the choice of neutralization reagent will affect the volume of sludge generated, the costs of sludge disposal, and the investment cost for storage and handling for each chemical. Because neutralization chemicals can affect the performance of existing neutralizers and gravity settling equipment, laboratory tests must be run in cooperation with vendors before changing chemicals. If a new system is being installed, the cost and performance analysis should be made during the design phase of the project.

Sodium hydroxide (caustic soda), lime, and soda ash are used as neutralization/precipitation agents (Table 8). Although lime and soda ash are much cheaper than caustic, their use requires more expensive feed systems. Lime is only slightly soluble in water. Soda ash is more soluble, but dissolves very slowly. Both usually are purchased in dry form and handled as slurries; this practice increases the capital costs for the associated neutralization feed systems. Because caustic is purchased as a liquid, the feed system is simpler and lower in cost. The plant, therefore, must evaluate the cost benefits of paying higher costs for neutralization chemicals or of adding capital for storage and handling facilities for lime or soda ash. Because soda ash is more expensive than lime, the plant usually will select between lime and caustic. These reagents therefore will be compared and discussed.

Table 8.
Cost Comparison of Common Alkaline Reagents

Agent	Chemical formula	Price ($/ton)	lb/lb H_2SO_4 neutralized	Relative cost	Process equipment required and sequence for use of reagents
Sodium hydroxide (caustic).....	NaOH	160 (98% NaOH equivalent)	0.826	6.83	Caustic storage → Neutralizer
Sodium carbonate (soda ash).....	Na_2CO_3	60 (58% Na_2CO_3)	1.90	5.89	Soda ash storage → Slurry tank → Neutralizer
High calcium hydrate (hydrated lime)....	$Ca(OH)_2$	34.50 (98% pure)	0.788	1.41	Hydrated lime storage → Slurry tank → Neutralizer
High calcium lime (quicklime)	CaO	32.50 (98% pure)	0.595	1.00	Quicklime storage → Slaking → Slurry tank → Neutralizer

Lime has a solubility in water of approximately 1 percent. It must be fed as a slurry, and, because of its low solubility, a 10 to 25 percent excess is required for complete neutralization. The hydrated lime feed system would be identical to the quicklime (CaO) system, except that the slaking equipment would not be required. The additional investment in slaking equipment (approximately $10,000 to $15,000) is typically justified if quicklime use requirements exceed 3 tons (2.7 Mg) per day. The additional capital investment required for a hydrated lime feed system over that required for a caustic feed system varies considerably, but the investment should be considered if requirements exceed 0.5 tons (0.45 Mg) per day of hydrated lime. Heavy metal precipitates resulting from lime neutralization will have superior settling and dewatering characteristics compared with those resulting from precipitation using caustic soda. The lime sludge will have a granular nature, primarily because of the presence of the calcium solids; caustic soda use will result in a fluffy, gelatinous floc. Consequently, lime treatment can improve the performance of clarification chambers and sludge dewatering equipment, thereby reducing the required size of these units.



Note.—Lime consumption is 20% in excess of neutralization requirements. 10% of $Ca(OH)_2$ addition remains insoluble and adds to sludge quantity. Initial pH of wastewater is 4.0. No insoluble calcium byproducts are formed.

Figure 18.
Solids Generation Using Lime or Caustic for Neutralization

As shown in Figure 18, lime wastewater treatment produces a greater quantity of dry solids than does caustic neutralization. The additional solids result from unreacted calcium hydroxide, insoluble compounds contained in the lime feed, and calcium byproducts of the treatment reactions, which precipitate because of their low solubility. Insoluble byproducts usually precipitate only when high lime doses are required for treatment; treatment of wastewater with a pH greater than 2 should not result in calcium byproduct precipitation.

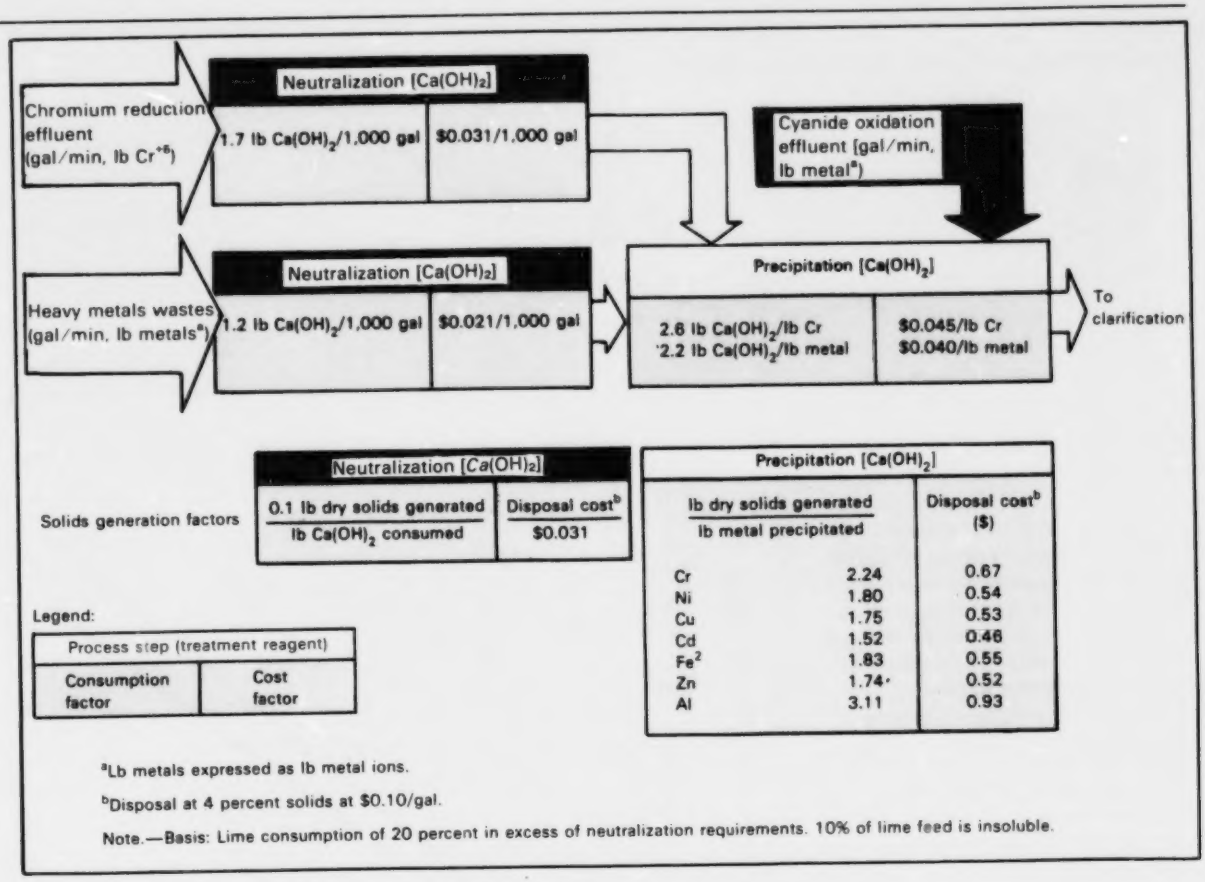
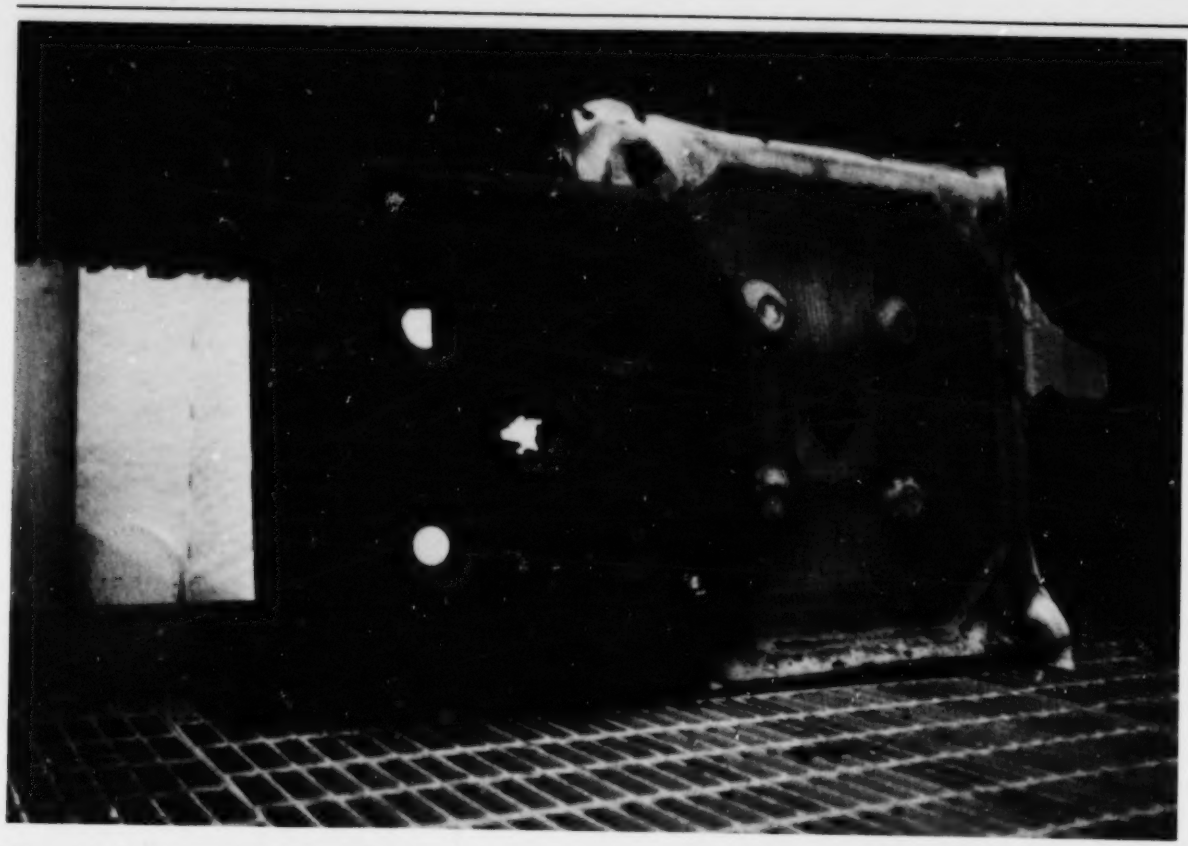


Figure 19.

Consumption and Cost Factors Using Lime for Wastewater Treatment

The lime requirements and chemical and sludge disposal costs can be estimated by using Figure 19, which is similar to the models developed in Figures 11 and 12 for caustic neutralization. Because sludge solids concentrations differ for lime and caustic, settling tests must be run to compare accurately the total costs of the two reagents. Using the wastewater flow rates and pollutant loading shown in Figure 13, the chemical cost for neutralization and precipitation using lime would be $2,400 per year, as compared with $9,000 per year for caustic. If the sludge is disposed at 4 percent solids and $0.10/gal in both cases, the disposal cost using lime will be $23,400 per year compared with $19,300 for caustic.



Filter plate and dewatered sludge cake

Sulfide Precipitation

Recently, with the more stringent control of the dissolved metal content of the wastewater effluent, the use of reagents to precipitate metals as sulfides has increased. Sulfide precipitation is capable of reducing the solubility of heavy metals to much lower concentration levels. Table 9 compares the solubilities of metal sulfides with the corresponding hydroxides. The sulfide process has other advantages, which include the following:

- The need for separate hexavalent chromium reduction is eliminated. The sulfide will reduce the Cr^{+6} to its trivalent state; as Cr^{+3}, under proper pH conditions, it will precipitate as the hydroxide.

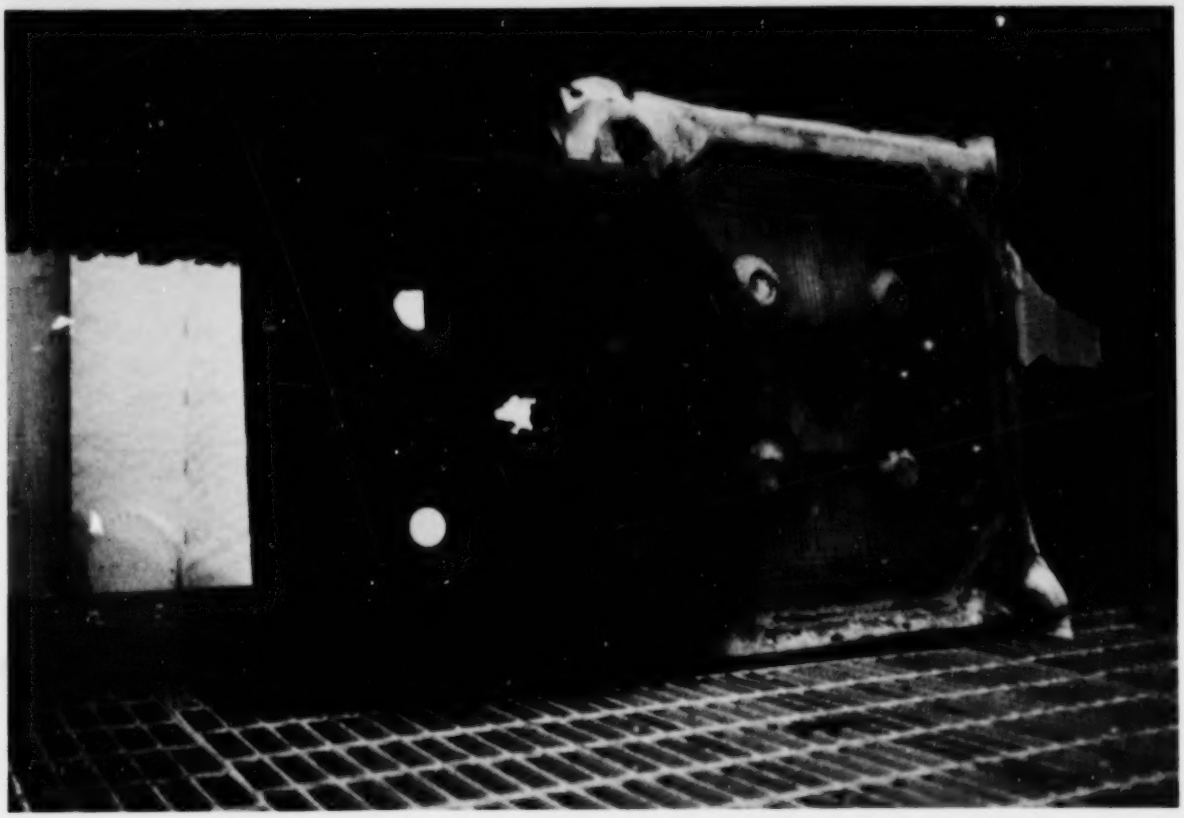
Table 9.

Solubility of Metals when Precipitated at pH 8.0 as Hydroxides and Sulfides

Metal	Solubility (mg/l)		Magnitude[a] of solubility difference
	Hydroxide	Sulfide	
Iron	2.2×10^{-15}	1.4×10^{-4}	−10.79
Nickel	1.2×10^{2}	3.3×10^{-6}	+2.55
Zinc	7.8×10^{-1}	1.0×10^{-6}	+5.92
Cadmium	2.8×10^{3}	1.0×10^{-8}	+11.46
Tin	1.7×10^{-11}	3.8×10^{-8}	−3.34
Lead	2.5×10^{2}	5.8×10^{-9}	+6.64
Copper	1.4×10^{-3}	1.8×10^{-13}	+9.96
Mercury	6.0×10^{-9}	1.3×10^{-21}	+12.66
Silver	2.2×10^{3}	5.4×10^{-12}	+20.62

[a]Positive magnitude (+) indicates lower solubility of sulfide salts than hydroxide salts.

SOURCE: *Lange's Handbook of Chemistry*, 11th ed., New York NY, McGraw Hill, 1973.



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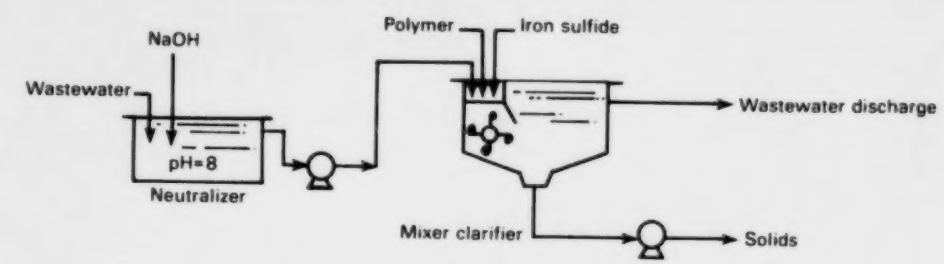
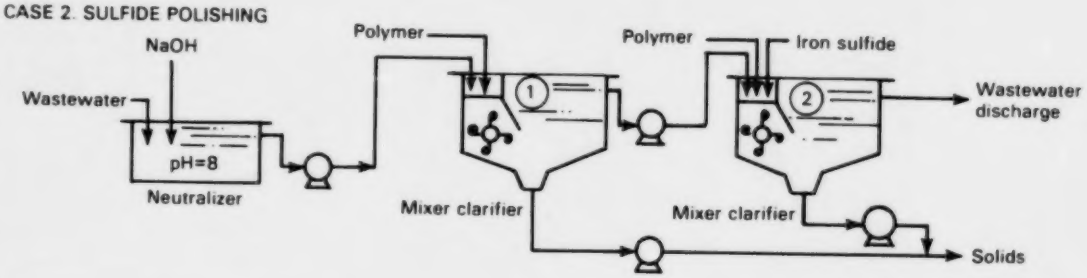
[a]Positive magnitude (+) indicates lower solubility of sulfide salts than hydroxide salts.

SOURCE: *Lange's Handbook of Chemistry*, 11th ed., New York NY, McGraw Hill, 1973.





	Waste stream	NaOH consumption (lb/h)	Neutralizer overflow	FeS[a] consumption (lb/h)	Solids[a] generated (lb/h)	Discharge	Cost ($) Treatment[a] chemicals	Cost ($) Sludge[a,b] disposal
Case 1	90 gal/min at 20 ppm Cr^{+6}, 10 ppm Cr^{+3}, 70 ppm Cu^{+2}, 60 ppm Zn^{+2}, 40 ppm Cd^{+2}	13.7	90 gal/min at 20 ppm Cr^{+6}, 0.8 ppm Cr^{+3}, 0.01 ppm Cu^{+2}, 0.8 ppm Zn^{+2}, 40 ppm Cd^{+2}	16.8	30.5	90 gal/min at 0.8 ppm Cr^{+3}, 0.01 ppm Cu^{+2}, 0.8 ppm Zn^{+2}, 0.01 ppm Cd^{+2}	13.84	9.15
Case 2	90 gal/min at 20 ppm Cr^{+6}, 10 ppm Cr^{+3}, 70 ppm Cu^{+2}, 60 ppm Zn^{+2}, 40 ppm Cd^{+2}	13.7	90 gal/min at 20 ppm Cr^{+6}, 0.8 ppm Cr^{+3}, 0.01 ppm Cu^{+2}, 0.8 ppm Zn^{+2}, 40 ppm Cd^{+2}	4.5	(1) 9.4 (2) 8.3 17.7	90 gal/min at 0.8 ppm Cr^{+3}, 0.01 ppm Cu^{+2}, 0.8 ppm Zn^{+2}, 0.01 ppm Cd^{+2}	3.44	5.31

[a]Based on iron sulfide consumption of 50 percent in excess of stoichiometric requirements.

[b]Disposal at 4 percent solids, $0.10/gal.

Figure 20.

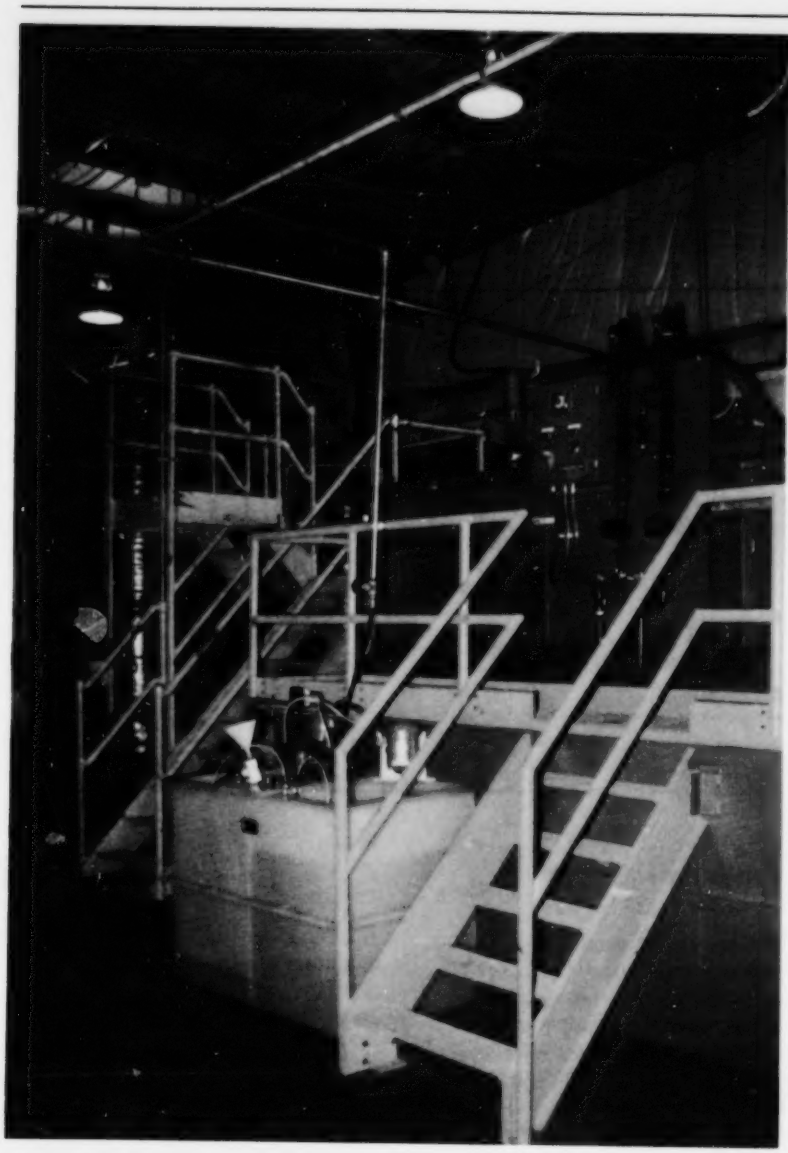
Sulfide Waste Treatment

- Sulfide precipitation, unlike hydroxide precipitation, is relatively insensitive to the presence of most chelating agents and eliminates the need to treat these wastes separately.
- Sulfide precipitation performs well on many complexed heavy metals.

In practice, sulfide precipitation is accomplished by one of two processes. In the soluble sulfide process, a probe that measures the concentration of sulfide ions is used to control the addition of soluble sulfides, such as sodium sulfide or sodium hydrosulfide. In the insoluble sulfide process, an excess of ferrous sulfide is added to the wastewater. The iron will give up its sulfide and precipitate any metal that has a lower solubility than the ferrous sulfide (Table 9). Under alkaline conditions, the iron will then precipitate as the hydroxide.

In practice, the sulfide process is used mainly as a polishing system after hydroxide precipitation to further reduce the solubility of the dissolved metals in the wastewater effluent. Figure 20 shows two approaches to using sulfide precipitation to augment an existing hydroxide neutralization system.

The first approach (Case 1) requires a minimum investment to achieve the treatment benefits of sulfide precipitation. It only requires the installation of a chemical feed system to add



Polymer addition tank with treatment system in background

the insoluble sulfide to the mixing zone of the clarifier or flocculator. This approach will require enough iron sulfide both to precipitate the remaining dissolved metals and to convert the precipitated metal hydroxides to metal sulfides. Consequently, iron sulfide consumption is high, and a large volume of metal sulfide and iron hydroxide sludge results.

The second approach (Case 2) requires a second clarifier to remove the precipitated metal hydroxides before sulfide precipitation. For large or moderate flows, the savings in treatment chemicals and disposal costs may justify this approach.

The costs of sulfide precipitation presented in Figure 20 for treatment chemicals and sludge disposal should not be considered additional treatment costs. For both cases, if sulfide treatment were not used to reduce the hexavalent chromium and to precipitate the dissolved cadmium, the wastewater containing these compounds would have to be treated separately before the neutralizer.

The least expensive treatment system can be determined by comparing the capital and operating costs for each approach. To determine the costs for a sulfide polishing system, use the cost presented in Figure 5 for installing a mixer clarifier; the costs for the feed systems to introduce the polymer and the insoluble sulfide are in the range of $2,200 to $4,000 each.

Sulfide precipitation is a relatively new approach for removal of heavy metals from the waste streams. The long-term stability of the sulfide sludge has not been determined, nor have the precautions for its safe disposal been defined.

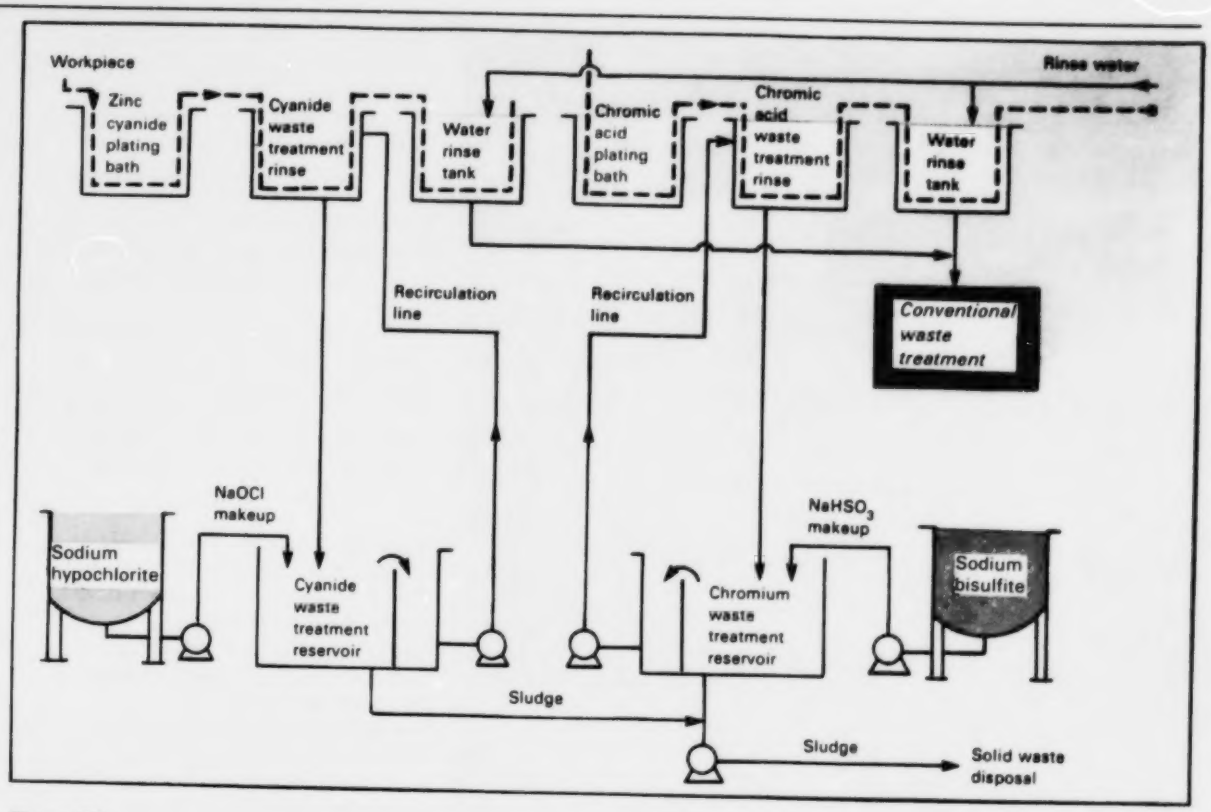


Figure 21.

Integrated Treatment for Chromium and Cyanide Plating Rinse Water

Integrated Wastewater Treatment

For the pollutants that require special treatment before neutralization—for example, chromium reduction and cyanide oxidation—it is possible to achieve operating costs and investment savings by incorporating the waste treatment step as part of the plating operation. In systems using this approach, the drag-out on the workpiece is treated in a rinse tank containing the treatment chemicals. Consequently, the drag-out is not diluted with rinse water before treatment. When the contaminated rinse water can be treated in a common neutralization/precipitation and gravity settling process, the use of multiple integrated systems may require additional capital, although the operating cost savings may still favor the integrated treatment approach.

An integrated wastewater treatment system for both chromium and cyanide drag-out is shown in Figure 21. The treatment tanks prohibit pollutants from entering the rinse tanks. The chemical reactions and treatment chemicals are identical to the conventional approaches (see Figure 1). No controls are required, however, because the workpiece is dipped directly into a rinse tank containing a concentrated solution of treatment chemicals. The workpiece is then rinsed with fresh water to cleanse the surface of any treatment chemicals or treated pollutants. The overflow from the water rinse tank is discharged to the neutralizer. The overflow from the treatment rinse tanks enters a treatment reservoir where makeup chemicals are added and the suspended solids settle out of solution.

The installed costs of integrated treatment systems are typically site specific. The hardware requirements shown in Figure 21 would include:

- Chemical rinse tank
- Chemical treatment reservoir
- Treatment solution recirculation pump and piping
- Sludge draw-off pump and piping
- Treatment chemical storage tank and feed system

As an alternative to conventional treatment systems, the integrated system approach can offer a significant investment cost savings. The installed cost for an integrated

system can be estimated using the data in Figures 22 and 23 for pumps and in Figure 24 for tanks. Assuming no extraordinary installation costs (such as new building space or relocation of existing equipment) are involved, each of the integrated systems pictured in Figure 21 should cost between $10,000 and $12,000. Often a plant will connect several waste treatment rinses of the same type to one common treatment reservoir. The costs for integrated treatment systems compare favorably with the investment cost required for conventional chromium reduction and cyanide oxidation systems presented in Figures 2 and 3.

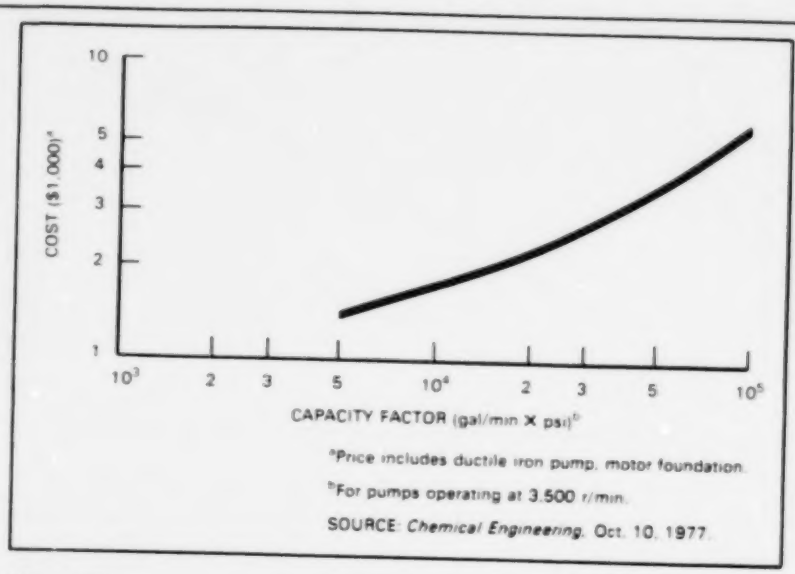


Figure 22.

Hardware Cost: Centrifugal Pumps

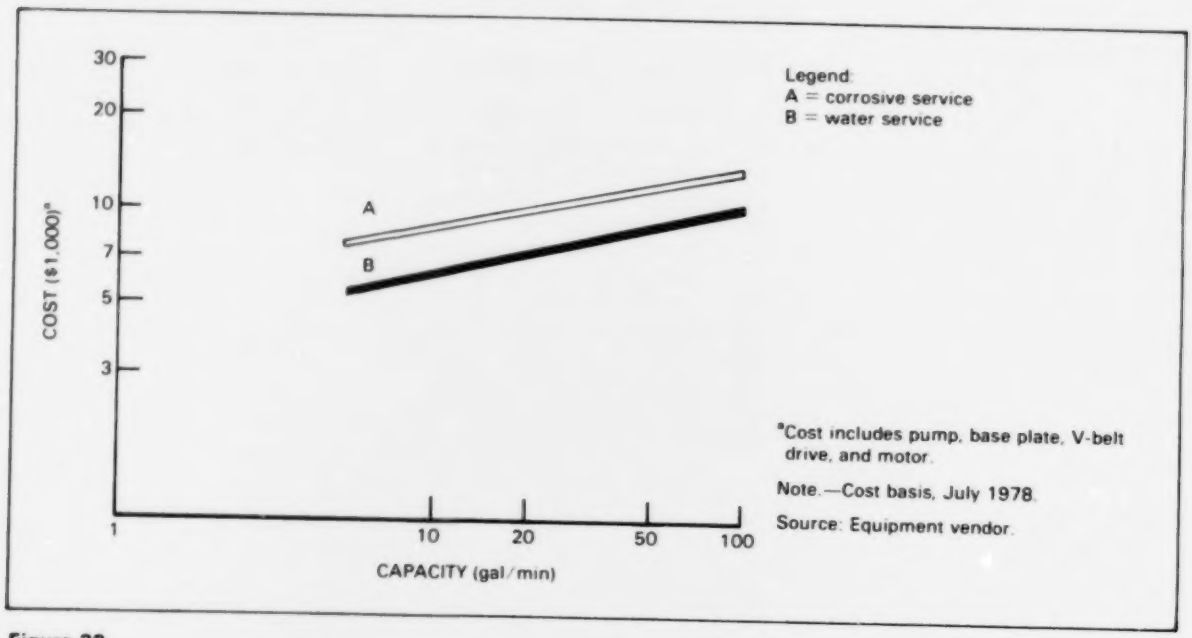


Figure 23.

Hardware Cost: Positive Displacement Pumps

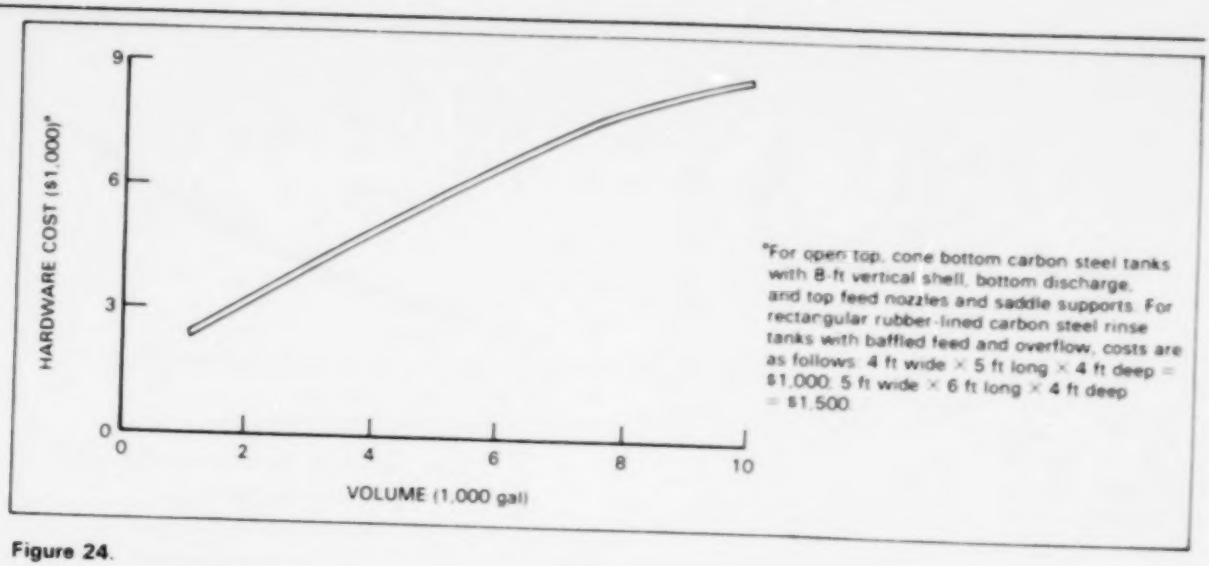

HARDWARE COST ($1,000)*
9
6
3
0
0
2
4
6
8
10
VOLUME (1,000 gal)
*For open top, cone bottom carbon steel tanks with 8-ft vertical shell, bottom discharge, and top feed nozzles and saddle supports. For rectangular rubber-lined carbon steel rinse tanks with baffled feed and overflow, costs are as follows: 4 ft wide × 5 ft long × 4 ft deep = $1,000; 5 ft wide × 6 ft long × 4 ft deep = $1,500.

Figure 24.

Hardware Cost: Tanks

The chemical use for a typical integrated treatment system can be determined from the composition of the plating bath and the volume of drag-out. The total treatment chemical cost should be approximately the same as that incurred in the conventional treatment systems. There will be some savings of acid and alkali required to adjust the rinse water pH in the conventional treatment systems. These savings should not be a significant factor, however, because the wastewater flow rates of these streams are usually low.

Other advantages of the integrated treatment approach include the following:

- The sludge generated is segregated in individual treatment reservoirs. Mixing of sludges does not occur and recovery or disposal of hazardous sludges in smaller volumes is possible. Currently, nickel is being recovered from an integrated treatment sludge by a plating chemical supplier, who in turn gives the sludge generator a purchase credit for the nickel value. This practice should become more widespread and should be applied to other plating materials in the future.
- The sludge formed in integrated treatment systems usually settles to a higher solids concentration because of its precipitation in the concentrated chemical solution. This effect will decrease the volume of sludge and reduce disposal costs.

4. Reducing the Costs of Wastewater Treatment

General

The operating and investment costs for wastewater treatment systems were shown to depend directly on the quantity of pollutants and on the volumetric flow rate of the wastewater. In-plant modifications to the plating baths and rinse systems can reduce wastewater flow rates and pollutant loading, and thereby can improve raw material yields and reduce pollution control costs. The methods described in this section are usually cost-effective alternatives to end-of-pipe wastewater treatment.

Housekeeping Practices

Implementing a successful housekeeping program as a rule requires little or no capital investment. As shown in Figure 25, the raw material and wastewater treatment savings can be significant, especially when loss of concentrated solutions of plating chemicals is prevented. Although substantial savings can be achieved by a housekeeping program, they can be easily lost unless routine surveillance procedures are implemented.

Major corrective actions would include:

- Repair leaks around processing equipment (tanks, valves, pump seals, transfer lines, heating coils, etc.). Losses of 2 gal/h (7.6 l/h) can occur easily through leaking pump seals alone.
- Install antisiphon devices, equipped with self-closing valves, on inlet water lines where warranted.
- Inspect tanks and tank liners periodically to avoid failures that might severely overload the waste treatment system.
- Inspect plating racks frequently for loose insulation that would cause excessive drag-out of plating solutions.
- Ensure that cyanide solutions do not mix with compounds (iron, nickel) that would form difficult-to-treat wastes.
- Use dry cleanup, where possible, instead of routine flooding with water.
- Install drip trays and splash guards where required.

For example, Figure 25 shows that correcting an average loss of 1 gal/h (3.8 l/h) from cyanide and chromium tanks (curves 1 and 5, total $15,000 loss) and 2 gal/h (7.6 l/h) from caustic soda storage (curve 4, total $5,000) would reduce the operating costs by $20,000 per year.

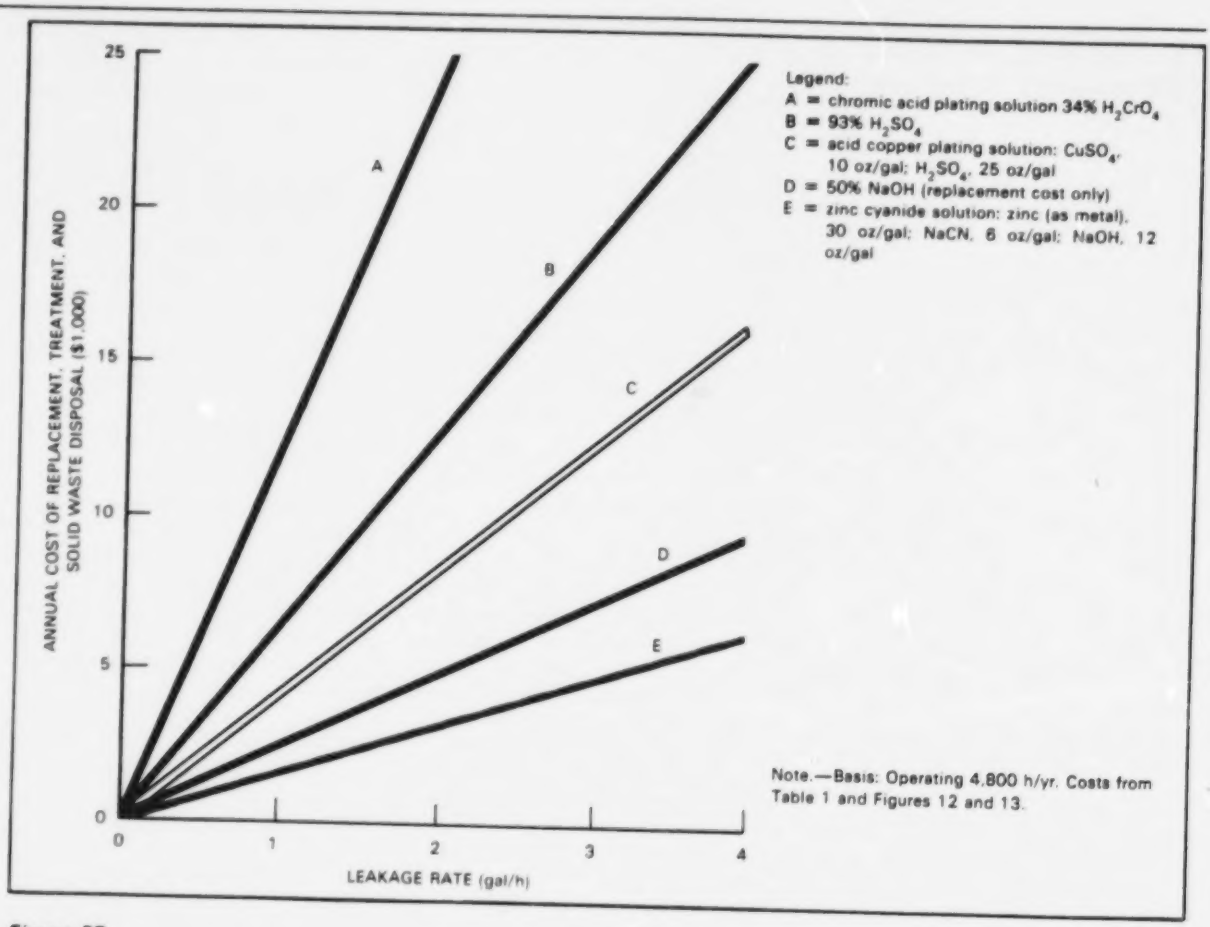


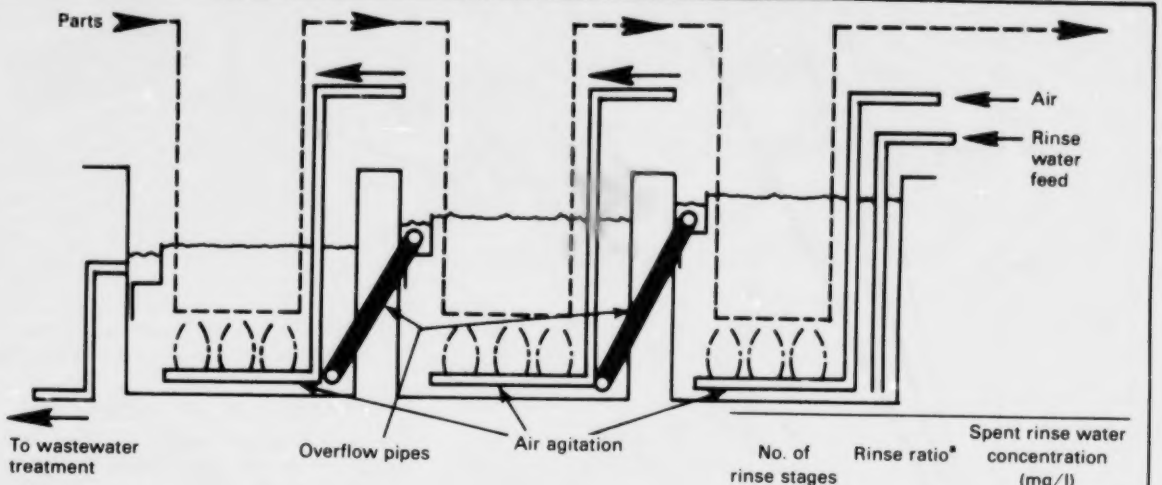
Figure 25.

Annual Cost of Chemical Leakage into Waste Treatment System

Minimizing Water Use

General. Major savings in treatment chemicals, sewer fees, and investment costs for wastewater treatment are achievable by conserving water. The major demand for water (as much as 90 percent) is in the rinse tanks that follow the different plating process steps. Consequently, the greatest potential for reducing wastewater flow rates is in these tanks. EPA has not determined whether to regulate pollution discharges based on an allowable quantity of pollutant per some production related parameter, or on pollutant concentration in the waste stream. If the former, minimizing the volume of water discharged will be a necessary step to comply with these regulations. Furthermore, if a plant is able to reduce its process water discharge to below 10,000 gal/d (37,850 l/d), it probably will be classified as a "small plater" and be regulated by different pretreatment standards. (This size criterion only applies to plants discharging to a publicly owned treatment works.)

Reducing Rinse Water Rates. Rinsing is used to dilute the concentration of contaminants adhering to the surface of a workpiece to an acceptable level before the workpiece passes on to the next step in the plating operation. The amount of water required to dilute the rinse solution depends on the quantity of chemical drag-in from the upstream rinse or plating tank, the allowable concentration of chemicals in the rinse water, and the contacting efficiency between the workpiece and the water.



THREE—STAGE COUNTERCURRENT RINSE WITH OUTBOARD ARRANGEMENT

No. of rinse stages	Rinse ratio*	Spent rinse water concentration (mg/l)
1	1,000	37
2	100	370
3	10	3,700
4	6	6,170

*Required to maintain concentration in final rinse at 37 mg/l if the drag-out concentration equals 37,000 mg/l.

Figure 26.

Rinse Water Rates Required and Effluent Concentration for Counterflow Rinse Systems

Various techniques are used in the electroplating industry to reduce the volume of water needed to achieve the required dilution, including:

- Installing multiple rinse tanks after a processing bath to reduce the required rinse rate drastically
- Subjecting the workpiece to a spray rinse as it emerges from the process tank to reduce the quantity of chemicals adhering to the workpiece and thereby the quantity of water needed for dilution
- Using conductivity cells to control water addition to rinse tanks and avoid excessive dilution of the rinse water
- Installing flow regulators on rinse water feed lines to control the addition rate at the minimum amount required
- Reusing contaminated rinse water where feasible.

If multiple rinse tanks are installed after the process bath where the rinse flows in a direction counter to that of the parts movement (Figure 26), the quantity of chemicals entering the final rinse will be significantly reduced compared with that entering a single-tank rinse system. The amount of rinse water required for dilution will be reduced by the same degree; the volume can be predicted for each rinse step by the use of a model that assumes complete rinsing of the workpiece. The ratio, r, of rinse water volume to drag-out volume is approximated by

$$r = (C_p/C_n)^{1/n}$$

where

C_p = concentration in process solution
C_n = required concentration in last rinse tank
n = number of rinse tanks

This model does not predict required rinse rates accurately when the value of r falls below 10. Also, complete rinsing will not be achieved unless there is sufficient residence time and agitation in the rinse tank.

The volume of rinse water required as a function of initial concentration in the plating bath, required concentration in the final rinse tank, and number of rinse tanks are shown in Figure 27. For example, a typical Watts-type nickel plating solution contains 270,000 mg/l of total dissolved solids, and the final rinse must contain no more than 37 mg/l of dissolved solids. The ratio of C_p/C_n is 7,300, and approximately 7,300 gallons (27,630 liters) of rinse water are required for each gallon of process solution drag-in with a single-tank rinse system. By installing a two-stage rinse system, water requirements are reduced to 86 gallons (326 liters) of water per gallon of process solution

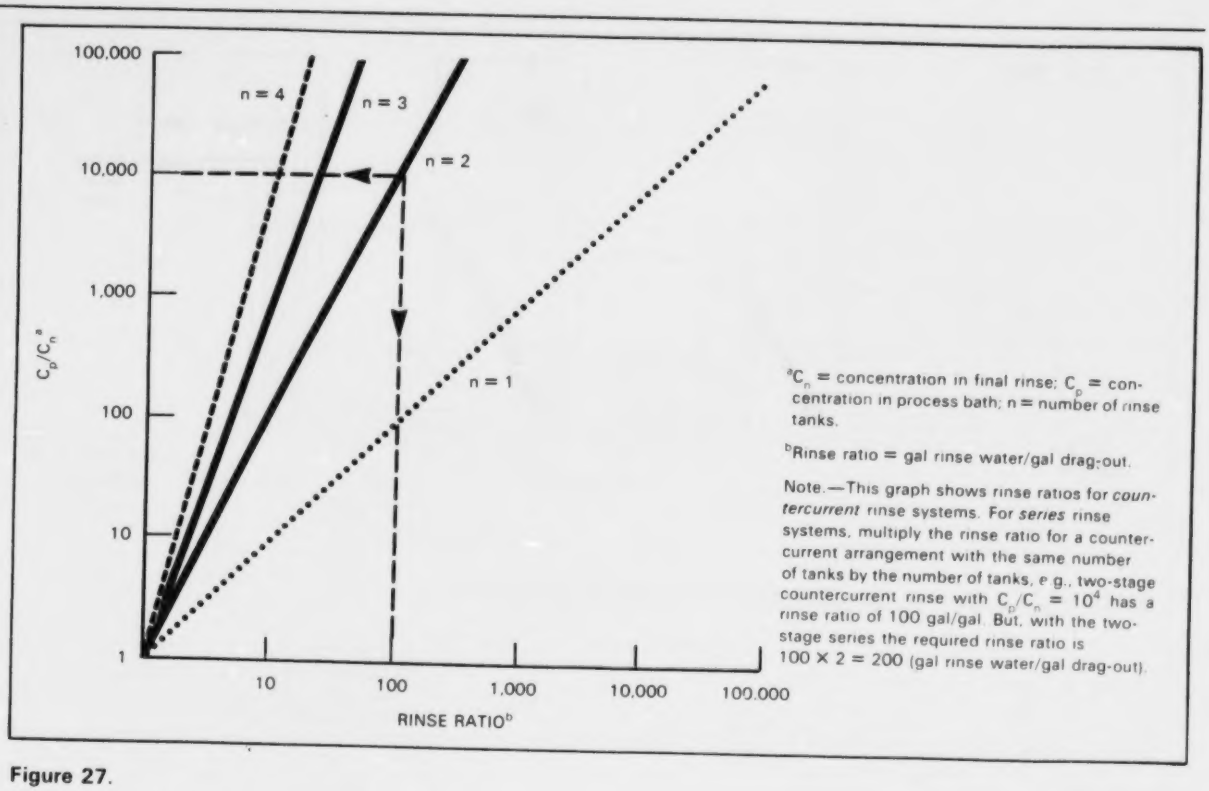

100,000
10,000
1,000
100
10
1
C_p/C_n[a]
n = 4
n = 3
n = 2
n = 1
10
100
1,000
10,000
100,000
RINSE RATIO[b]
[a]C_n = concentration in final rinse; C_p = concentration in process bath; n = number of rinse tanks.
[b]Rinse ratio = gal rinse water/gal drag-out.
Note.—This graph shows rinse ratios for *countercurrent* rinse systems. For *series* rinse systems, multiply the rinse ratio for a countercurrent arrangement with the same number of tanks by the number of tanks, e.g., two-stage countercurrent rinse with $C_p/C_n = 10^4$ has a rinse ratio of 100 gal/gal. But, with the two-stage series the required rinse ratio is 100 × 2 = 200 (gal rinse water/gal drag-out).

Figure 27.

Estimating Rinse Ratios Based on Drag-Out and Final Rinse Concentration for Multiple-Tank Rinse Systems

drag-in. The same degree of dilution is obtained in the final rinse, and the rinse water consumption is reduced by 99 percent. The mass flow of pollutants exiting the rinse system remains constant.

If this bath had a drag-out rate of 0.5 gal/h (1.9 l/h), the single rinse tank would require 3,650 gal/h (13,820 l/h) of rinse water (0.5 × 7,300). A three-stage countercurrent rinse arrangement would reduce water consumption from 3,650 gal/h (13,820 l/h) to 10 gal/h (38 l/h) (0.5 × 20). The resulting cost benefits would include reducing water use and sewer fees by $4/h (based on $1.10/1,000 gal combined water use and sewer fees) and reducing the size of the required waste treatment systems, which are designed on the basis of volumetric flowrate.

The investment cost to add two additional rinse tanks is highly site specific; for manual plating operations the major factor affecting cost would be the availability of space in the process area. For automatic plating machines, the cost of modifying the unit to add additional stations may be as high as $20,000 per station. Costs for the rinse tanks are given in Figure 24 for rubber-lined steel open top tanks with appropriate weir plates and nozzles. The cost, excluding installation, is in the range of $1,000 to $1,500, depending on cross-sectional area required for the workpiece.

A series rinse arrangement also can be used with multiple rinse tanks. In this case, each rinse tank receives a fresh water feed and discharges the overflow to waste treatment. The rinse ratio required for a series rinse arrangement is defined by $r = n(C_p/C_n)^{1/n}$ If the rate given in Figure 27 for a countercurrent rinse system with the same number of rinse tanks is multiplied by the number of rinse tanks, the series rinse water rate can be estimated. Rinse water rates are significantly higher for series rinsing.

A conductivity probe is another effective water-saving device to use in rinsing systems. Except on highly automated plating machines, the frequency of rinse dips generally varies considerably. Because the fresh rinse water usually is fed continuously, there are periods of excess dilution and, consequently, of excess water being used. A conductivity cell measures the level of dissolved solids

in the rinse water and, when the level reaches a preset minimum, it shuts a valve interrupting the fresh water feed. When the concentration of dissolved solids builds up to the maximum allowable level, it opens the valve. Thousands of these units are used throughout industry because they are so reasonable in price. A complete set, including a probe, controller, and automatic 1-inch (2.5-cm) valve can be purchased and installed for $200 to $1,000.

A further water conservation step employs flow regulators as a means of controlling the fresh water feed within a narrow range despite variations in line pressure. These devices also eliminate the need to reset the flow each time the valve is closed. They also have been designed to act as syphon breakers and aerators (by the venturi effect) and are provided in a wide range of flow settings. The units cost approximately $20 to $30.

Water Reuse. Reusing water is another method of reducing water use. In critical or final rinsing operations, the level of contaminants remaining on the workpiece must be extremely low; for some intermediate rinse steps, however, the level of contaminants can be higher. Water consumption can be reduced by reusing the contaminated overflow from the critical rinse in a rinse for which water specifications are less critical. Water also may be reused where the contaminants in rinse water after a processing step do not detract from the rinse water quality at another rinsing station. For example, the overflow from the rinse after an acid dip may be reused as the feed to rinse after an alkaline dip. Choosing the optimum configuration requires analyzing the particular rinse water needs. Interconnections between rinsing systems might make operations more complicated, but the cost advantage they represent justifies the extra attention they require.

Table 10.

Economic Penalty for Losses of Plating Chemicals

Chemical	Cost ($/lb)			
	Replacement	Treatment[a]	Disposal[b]	Total
Nickel:				
As $NiSO_4$	0.76	0.28	0.17	1.21
As $NiCl_2$	1.04	0.29	0.24	1.57
Zinc cyanide as $Zn(CN)_2$:				
Using Cl_2 for cyanide oxidation	1.41	0.72	0.25	2.38
Using NaOCl for cyanide oxidation	1.41	1.53	0.25	3.19
Chromic acid as H_2CrO_4:				
Using SO_2 for chromium reduction	0.78	0.48	0.32	1.58
Using $NaHSO_3$ for chromium reduction	0.78	0.69	0.32	1.79
Copper cyanide as $Cu(CN)_2$:				
Using Cl_2 for cyanide oxidation	1.95	0.72	0.25	2.92
Using NaOCl for cyanide oxidation	1.95	1.53	0.25	3.73
Copper sulfate as $CuSO_4$	0.56	0.28	0.17	1.01

[a]Based on treatment model presented in Figure 12 at a concentration of 100 mg/l in wastewater.

[b]Based on Figure 13.

Reducing Drag-Out Loss

General. As a workpiece emerges from a plating bath, it carries over a volume of plating solution into the rinse system. This carryover, known as drag-out, is usually the major source of pollutants in an electroplater's waste stream. Table 10 shows the economic penalty suffered for each pound of assorted plating chemicals lost to the waste stream. The cost of replacing the raw materials and treating and disposing of the waste is high; consequently, the cost effectiveness of modifications to minimize drag-out is very attractive.

Generally, one of two approaches can be used: reduction of drag-out before rinsing or recycling rinse water to the plating bath. Various percentages of recovery are achievable depending on the number of rinse tanks in the rinsing system, the concentration of pollutants permissable in the final rinse tank, and the volume of rinse water that can be recycled to the plating tanks. To assess the potential economy of drag-out recovery, the quantity of plating solution lost to the rinse system must be determined. A first approximation of this quantity can be derived by multiplying the quantity of plating chemicals added to the bath by an assumed loss factor. Typically for chrome plating operations, about 0.9 pound (0.4 kg) of chrome is lost as drag-out per pound added to the plating tank. The loss factors for other plating baths are between 50 and 90 percent.

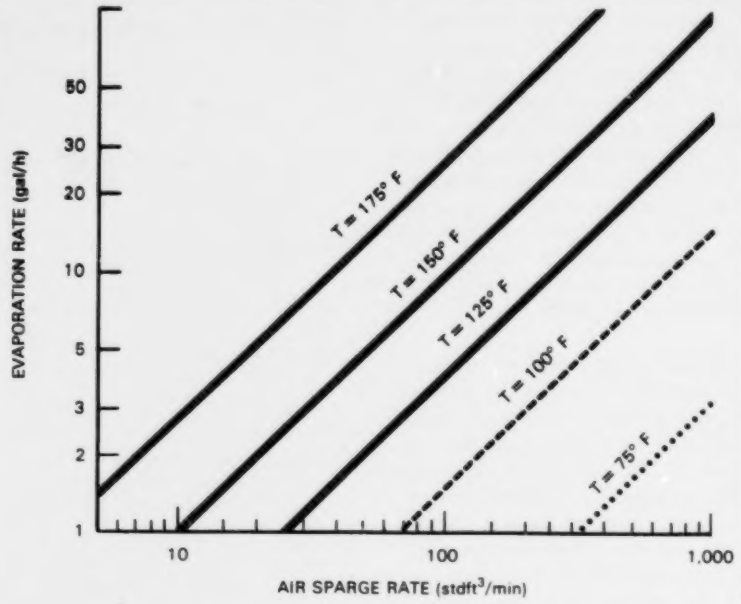
If the chemical loss represents a significant cost (Table 10), a more precise determination may be required to substantiate the benefits of investing in drag-out recovery modifications. The following five steps constitute the recommended analytical technique:

1. Fill the rinse station after the process bath with a known volume of water.
2. Using normal production procedures, plate and rinse a representative production unit.
3. Stir the rinse tank and collect a sample of rinse water.
4. Plate and rinse several additional production units and collect another sample of rinse water.
5. Repeat Step 4.

The rinse water samples then must be sent to a laboratory to determine the concentration of plating chemicals in the rinse. Multiplying the volume of rinse solution by the concentration of chemical will determine the quantity of chemical drag-in per production unit. The volume of drag-out per hour can be determined if the production rate and the chemical concentration of the plating solution are known.

Drag-Out Recovery from Rinse Tanks. The drag-out lost from the plating bath can be reduced significantly by usually low-cost recycle modifications after rinsing modifications are completed. As a rule these modifications are applicable to baths that have a considerable amount of surface evaporation. The rinse water containing dragged-out plating chemicals can be returned to the plating bath from the rinse tanks to make up for water lost by surface evaporation.

Low temperature baths have minimum surface evaporation and their temperature cannot be increased without degrading heat sensitive additives. Recently, new additives, which are not as readily heat degraded, have been developed for many of these plating baths. These additives might make operation of the plating bath possible at higher temperatures, facilitating drag-out recovery by recycle techniques. Usually, the value of the recovered chemicals is much greater than the increased energy cost associated with operating the bath at a higher temperature.



Note.—Supply air at 75° F, 75% relative humidity. Plating solution is 95% mole fraction H_2O.

T = plating bath temperature.

Figure 28.

Surface Evaporation Rate from Aerated Plating Baths

The evaporation rate determines the total volume of rinse water that can be recycled to the plating tanks. The quantity of the plating chemicals in the recycled rinse water represents the savings of plating chemicals previously lost to the pollution control system. If the required rinse water rate can be matched to the evaporation rate, no rinse water is discharged to waste treatment and the plating bath is operated as a closed-loop system.

The rate of surface evaporation for plating tanks with air agitation is shown in Figure 28; the rate for those without air agitation (surface evaporation only) is shown in Figure 29. If the use of air agitation significantly increases the evaporation rate, it also will significantly increase the heat loss from a plating tank and the energy cost to keep the bath at its operating temperature. Figure 30 presents the heat input required to compensate for heat loss resulting from the use of air agitation. The heat loss caused by surface evaporation in a plating bath without air agitation can be calculated from: Heat load (Btu/h) = surface evaporation (gal/h) × 8,300 (Btu/gal).

For example, two plating tanks, each with a 30-ft^2 (2.8-m^2) surface area, are operated at 150° F (66° C). One uses 100 stdft^3/min (2.8 normal m^3/min) air agitation, and the second operates without air agitation. The surface evaporation rates would be 9.8 gal/h (37.1 l/h) and 4.2 gal/h (15.9 l/h), respectively. The heat inputs required would be 107,500 and 34,860 Btu/h (31,505 W and 10,216 W), respectively. Using indirect steam heating to compensate for the heat loss would cost $0.32/h for the air agitated bath compared to $0.10/h for the bath without air agitation, based on an energy cost of $3/10^6 Btu.

Significant drag-out recovery can be achieved for each plating tank by using a multistage rinse system and returning the concentrated rinse water to the bath to compensate for the evaporation losses. If the required rinse water rate were equal to the evaporation rate, the entire volume of rinse water could be returned to the plating bath. For this case, the reduction of drag-out loss as compared to an operation with no recycle is given by the following formula:

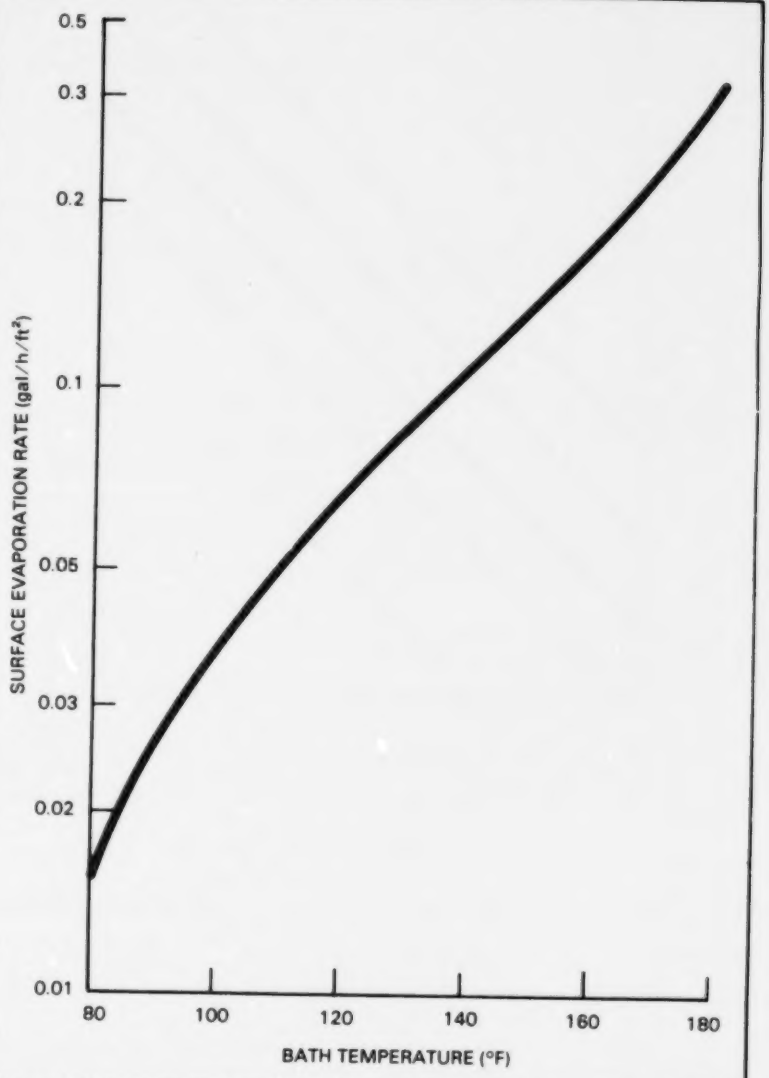
Percent recovery of drag-out

$$= \left(1 - \frac{C_n}{C_p}\right) \times 100\%$$

where:

C_p = concentrations in plating bath
C_n = concentrations in final rinse tank

The only loss is drag-out from the last rinse tank, which has a dilute concentration of plating chemicals.



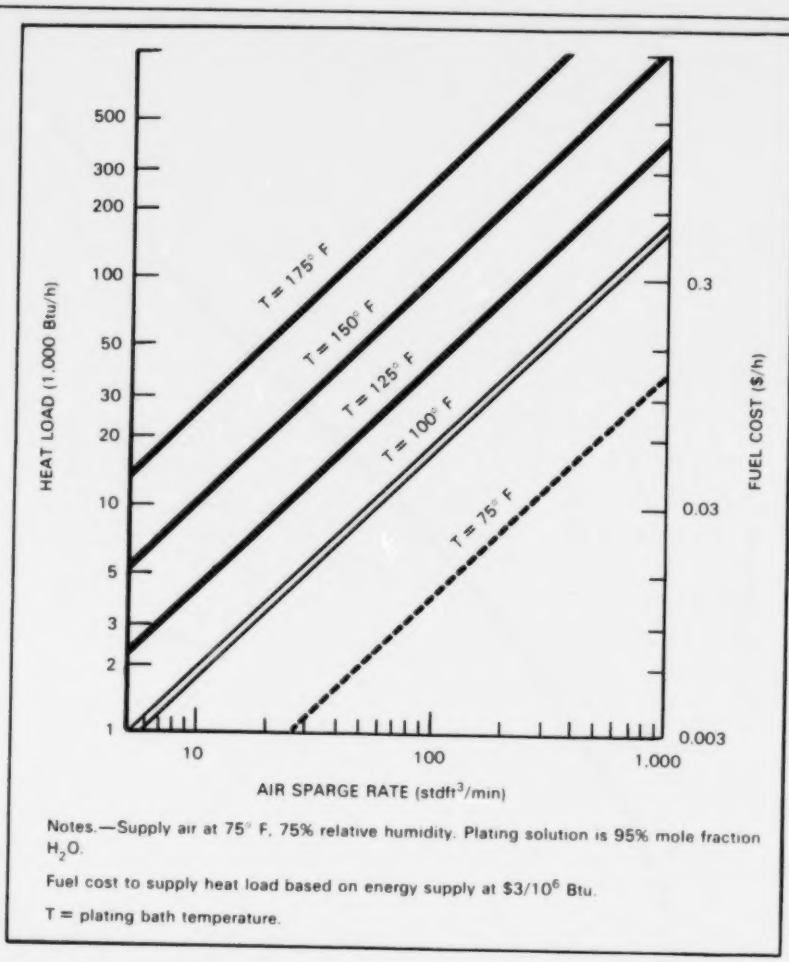
Note.—Ambient conditions are 75° F, 75% relative humidity. Plating solution is 95% mole fraction H_2O.

Figure 29.

Surface Evaporation Rate from Plating Baths with No Aeration

When a low final rinse concentration is required, excessive drag-out occurs, or surface evaporation is minimal, a closed-loop, countercurrent rinse-and-recycle system probably will be impractical because of the large number of rinse stages required.

By operating the final rinse in a multiple-tank system as a free rinse and using the upstream tanks as a countercurrent rinse-and-recycle system, significant drag-out recovery still can be realized while rinsing quality



Notes.—Supply air at 75° F, 75% relative humidity. Plating solution is 95% mole fraction H_2O.

Fuel cost to supply heat load based on energy supply at $3/10^6 Btu.

T = plating bath temperature.

Figure 30.

Heat Load Resulting from Aeration of Plating Baths

is maintained. Figure 31 depicts such a system, and Figure 32 defines the percent recovery of drag-out as a function of recycle ratio, which is the volume of recycled rinse divided by the volume of drag-out. The recycle rinse rate in the recovery rinse tanks is equal to the evaporation rate. The data presented in Figure 27 can be used to determine the required water rates for the final rinse once the concentration in the recovery rinse is known.

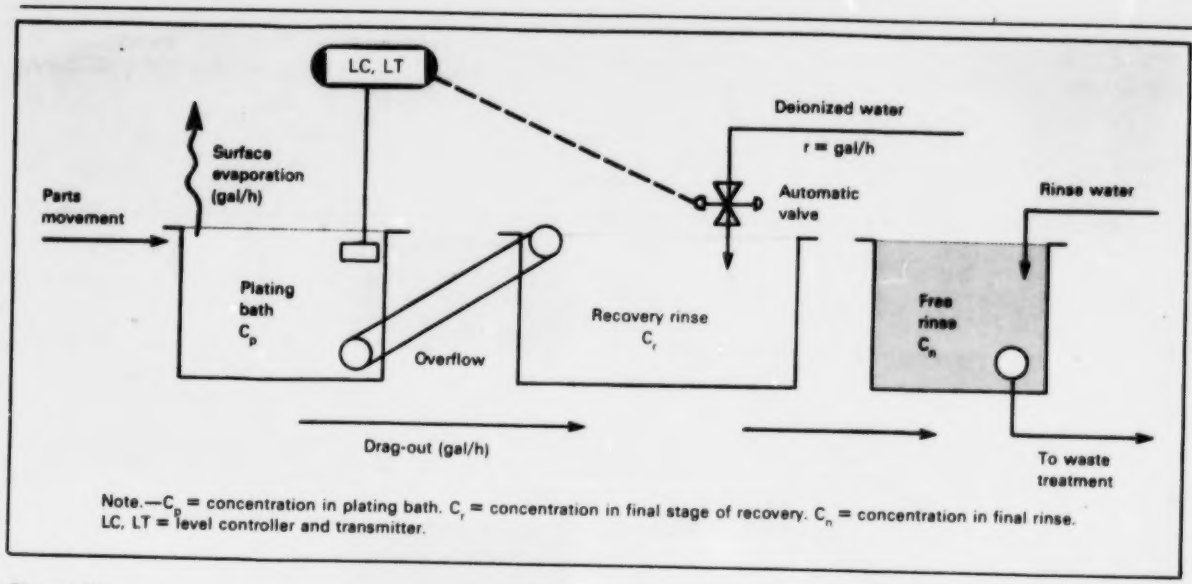
As an example, a nickel plating operation has these operating characteristics: a drag-out rate of 0.5 gal/h (1.9 l/h), a surface evaporation rate of 5 gal/h (19 l/h), and a final rinse concentration of 40 mg/l. Therefore, the recycle ratio could be set at 10. From Figure 29, a one-stage recovery rinse and recycle system would reclaim 91 percent of the drag-out (point A). At this recovery rate, the concentration ratio is 0.09. Assuming an initial plating tank concentration of 270,000 mg/l, the concentration entering the final rinse is 0.09 × 270,000, or 24,300 mg/l. The water requirements in the final rinse would be reduced by the same level as drag-out losses, when compared with the required rinse rates for a single-tank rinse system. The rinse water required in the final rinse tank, calculated by using Figure 27, is 304 gal/h (1,150 l/h).

The curves in Figure 32 were plotted assuming that water is added continuously to make up for surface evaporation losses. This practice may not be feasible and the water usually will be added in increments, resulting in cyclical movement along the curves presented in Figure 32. The longer the time interval between additions, the greater the variation in the recovery of the drag-out realized. Particularly at low recycle rates, where the recovery potential is very sensitive to changes in the recycle ratio, minimizing the time between additions will significantly increase the amount of drag-out recovered. A level control device will approach the potential of continuous water addition and is recommended if the recycle ratio is in the range of 3 or less. These control loops cost between $500 and $1,200.

Deionized water is specified for any rinse stream that is recirculated to the plating bath to avoid the progressive buildup of contaminants in the bath.

Reducing Drag-Out from Plating Tanks. Two effective methods of reducing the concentration or volume of plating solution lost from the plating tanks are spray rinses and air knives.

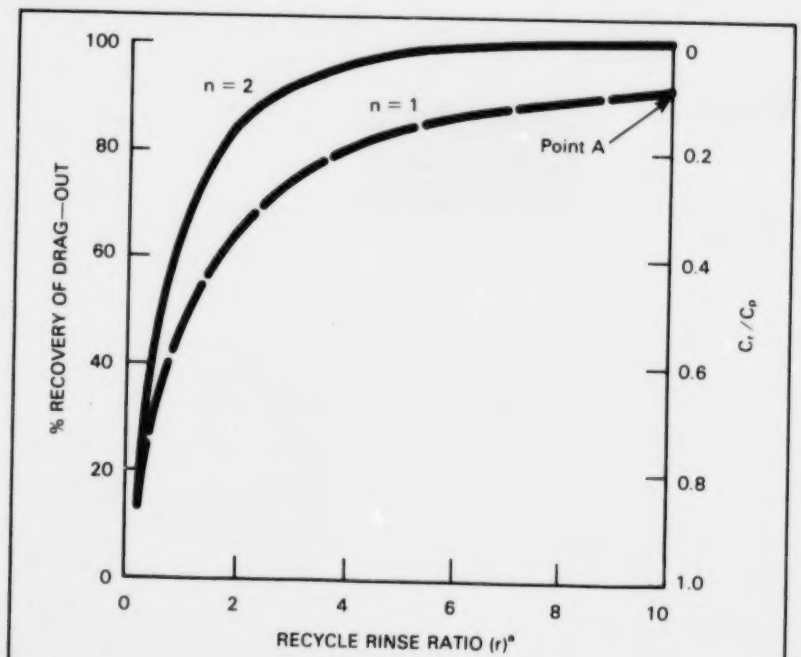
Spray rinses are ideal for reducing drag-out from the plating tank on automated lines. As the workpiece is withdrawn mechanically from the plating solution, a spray of water automatically washes the part, draining as much as 75 percent of the chemicals back into the plate tank. Again, the volume of spray rinse cannot exceed the volume of surface evaporation from the plate tank. Spray rinsing is best suited for flat parts, but will reduce drag-out effectively on any part plated.



Note.—C_p = concentration in plating bath. C_r = concentration in final stage of recovery. C_n = concentration in final rinse. LC, LT = level controller and transmitter.

Figure 31.

Rinse-and-Recycle Drag-Out Recovery



*r = recycle rinse (gal/h) ÷ drag-out (gal/h).

Note.—r (recycle rinse flow) = surface evaporation from bath. n = number of counterflow rinse tanks in recovery use.

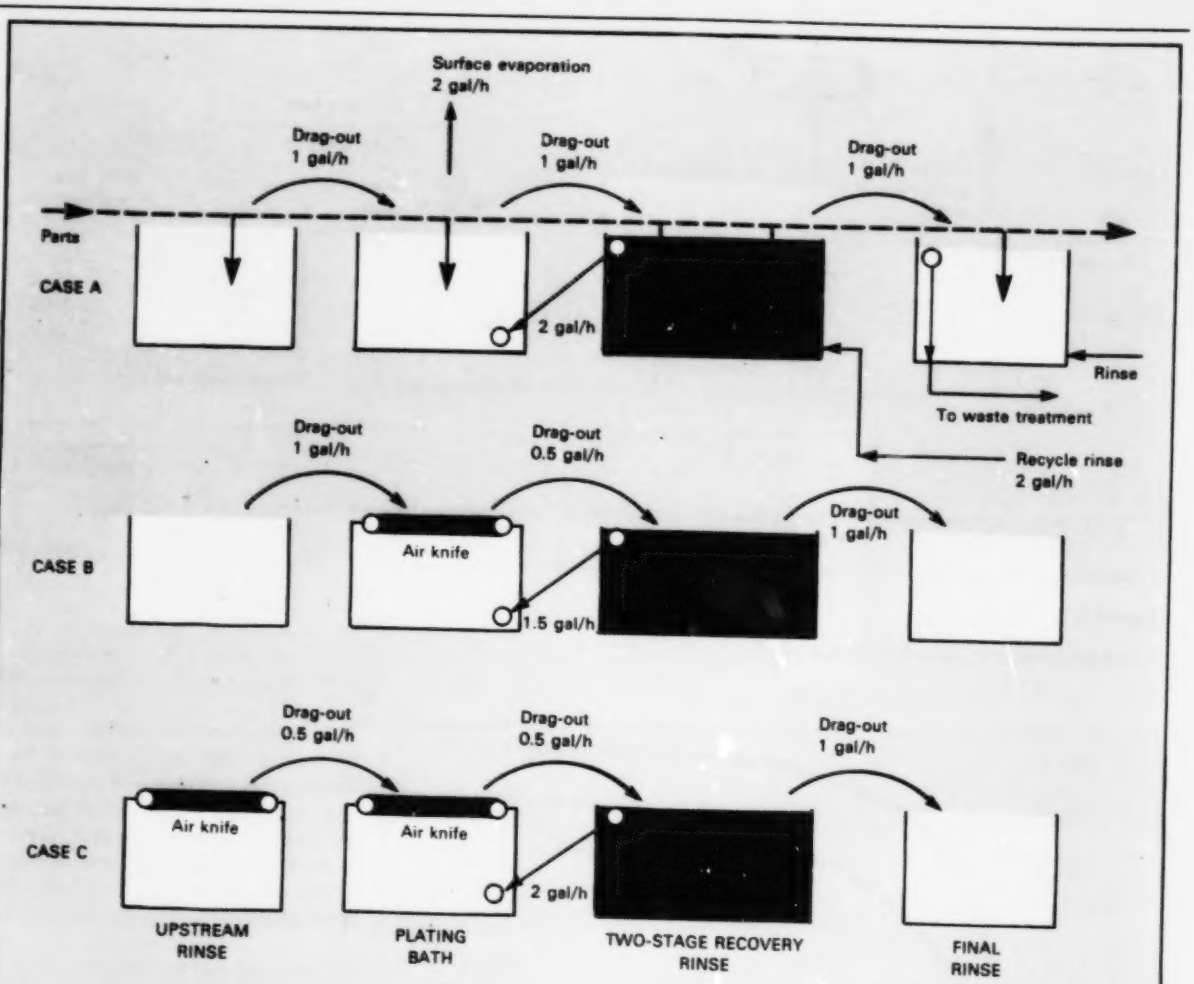
Figure 32.

Percent Drag-Out Recovery with Rinse-and-Recycle System

The savings are calculated in terms of the concentration change in the drag-out. For example, if the concentration of the drag-out were 100,000 mg/l and a spray rinse reduced the concentration to 50,000 mg/l, the chemical losses would be reduced by 50 percent.

An air knife can be used to reduce drag-out in much the same way as a spray rinse, particularly when the surface evaporation rate in the plating bath is low. The savings in operating costs are equal to the percent reduction in volume of drag-out adhering to the workpiece. The concentration of the dragged-out solution remains the same.

An air knife also can be used to improve the drag-out recovery of the rinse and recycle system (shown in Figure 31), which is characterized by a low recycle ratio. Installing an air knife (as shown in Figure 33) reduces the volume of drag-out from the plating bath from 1 to 0.5 gal/h (3.8 to 1.9 l/h). Also, the recycle rinse ratio of the recovery rinse is increased from 2 to 3, which increases recovery from 84 percent to 92 percent (Case B).



Chromium Plating Bath

Item	Case A	Case B	Case C
Modifications	—	Install air knife ring	Install two air knife rings
Plating solution drag-out	1 gal/h	0.5 gal/h	0.5 gal/h
Recycle rinse rate	2 gal/h	1.5 gal/h	2 gal/h
% drag-out recovery[a]	84%	92%	96%
Rinse water requirements in final rinse[b]	1,300 gal/h	650 gal/h	320 gal/h
% reduction in water use[b]	—	50%	75%

[a]From figure 32.

[b]C_n = 37 mg/l, from Figure 27.

Note.—Bath composition: 3.125 lb H_2CrO_4 per gallon.

Figure 33.

Impact of Air Knife on Drag-Out Recovery and Rinse Water Use

Further recovery of drag-out can be achieved by installing an air knife in the upstream rinse tank. The reduction in drag-in would increase the amount of recycle returned to the plating bath from the rinse system by an equal amount. Consequently, recovery potential would be increased (Figure 33, Case C).

Impact on Drag-Out Losses of Minimizing Bath Concentrations. In operations where a metal finish is applied to a surface by immersion of that surface in a chemical solution, the quantity of the chemicals removed from the bath is a function of the concentration in the solution and the quantity of solution carried over the edge of the bath by the emerging piece of work.

Traditionally, the midpoint within a range of operating concentrations is chosen for plating solutions. This practice derives from sound reasoning, as long as the incremental cost of the additional chemicals lost is less than the cost of more rigorous control procedures. Consider a standard nickel plating solution that has the concentration limits shown in Table 11.

A typical small plating shop that operated at an average of 12 h/d, 250 d/yr, and processed 600 ft^2/h (56 m^2/h) would lose 2,700 gal/yr (10,220 l/yr) of process solution attributed to drag-out, based on drag-out rate of 1.5 gal/1,000 ft^2 (61 l/1,000 m^2). Modifying the operating conditions to the minimum values indicated above would save this shop 390 pounds (177 kg) of nickel sulfate and 150 pounds (68 kg) of nickel chloride annually. The money saved in replacement chemicals, treatment costs, and sludge disposal (as shown in Table 10) would amount to $700 per year. The same type of assessment could be applied to any metal finishing operation.

Table 11.
Standard Nickel Solution Concentration Limits

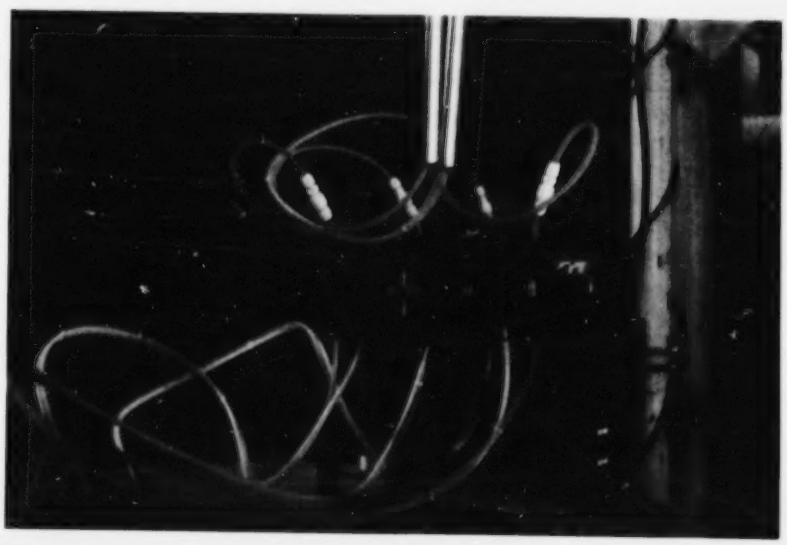
Chemical	Concentration range (oz/gal)	Operating condition (oz/gal)	Modified operating condition (oz/gal)
Nickel sulfate:			
$NiSO_4 \cdot 6H_2O$	40-50	45	41.0
As $NiSO_4$		26.5	24.2
Nickel chloride:			
$NiCl_2 \cdot 6H_2O$	8-12	10	8.5
As $NiCl_2$		5.5	4.6
Boric acid (H_3BO_3)	6-6.5	6.25	6.1

Using Spent Baths as Treatment Reagents

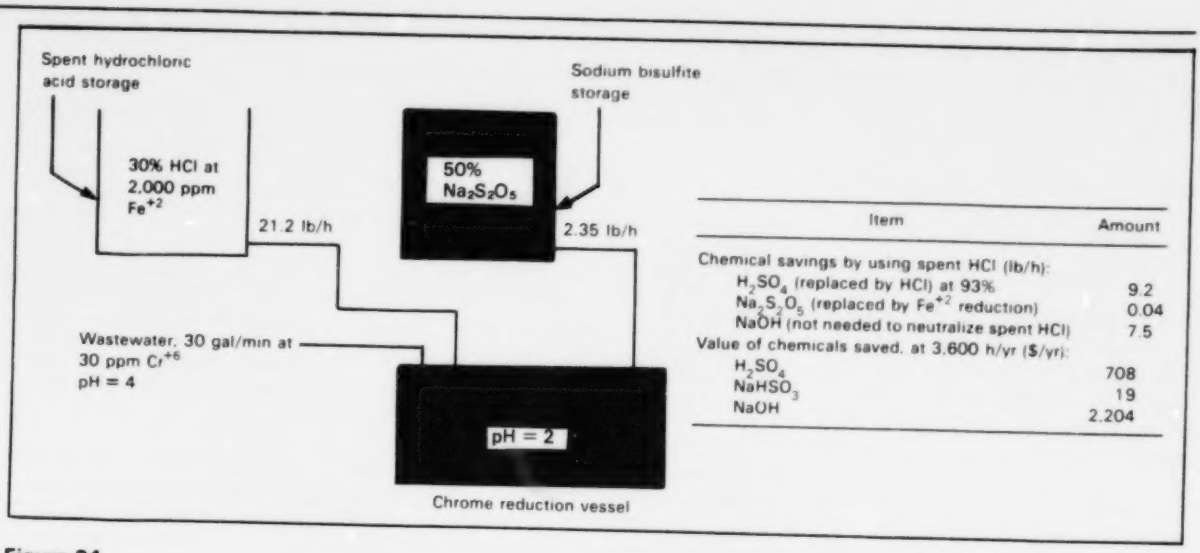
Often the processing solutions used in alkaline or acid cleaning steps of the electroplating process can be used as pH adjustment reagents in the waste treatment system. These baths are either dumped when the contaminant level exceeds some acceptable concentration or bled off to waste treatment and replaced with fresh reagents to maintain the concentration of contaminants below that level. In either case, the solution could be transferred to a holding tank instead, and could be used to treat the wastewater.

Spent caustic soda solutions can be used for pH adjustment in the neutralization/precipitation step. Spent sulphuric and hydrochloric acid solutions also can be used here, but because waste streams are usually acidic, the quantity used would be minimal.

Waste acid solutions (HCl, H_2SO_4) can be used for pH adjustment in the chrome reduction process (Figure 34). A minor added benefit in this case would be a decrease in the demand for reducing agent caused by the presence in the acid of any Fe^{+2} iron, which will reduce Cr^{+6}.



Acid feed pump with neutralizer in background



Item	Amount
Chemical savings by using spent HCl (lb/h):	
H_2SO_4 (replaced by HCl) at 93%	9.2
$Na_2S_2O_5$ (replaced by Fe^{+2} reduction)	0.04
NaOH (not needed to neutralize spent HCl)	7.5
Value of chemicals saved, at 3,600 h/yr ($/yr):	
H_2SO_4	708
$NaHSO_3$	19
NaOH	2,204

Figure 34.

Chemical Savings Resulting from Use of Spent HCl in Chrome Reduction Treatment

Further reduction in reducing agent demand could be achieved by dissolving scrap iron in the spent acid, thus raising the concentration of the Fe^{+2}. For each pound of sodium bisulphite reducing agent replaced with iron, however, an additional 1.7 pounds (0.77 kg) of iron hydroxide sludge will be generated. At a disposal cost of $0.10/gal, it will probably cost more to dispose of the additional solid waste than will be saved by reducing chemical consumption.

If additives are used to improve the properties of these spent solutions for their original function, the impact of the additives on the waste treatment process should be considered before they are used as treatment reagents.

Example of Cost/Benefits Analysis

Cost-Saving Examples. The potential savings in water and chemicals can be predicted using the data developed in this section. The example that follows illustrates application of these modifications to a typical nickel-chromium-plating operation. The worksheet provided in Appendix A can be used to develop a similar analysis for most plating shops.

The shop plates approximately 600 ft^2/h (56 m^2/h) in its nickel-chromium operation, operating an average of 10 h/d, 300 d/yr. Figure 35 shows the processing sequence and water use rates for the operation. The original processing sequence used two-stage countercurrent rinse systems after the nickel and chromium plate tanks. As shown in Figure 36, in-plant modifications were made at six locations (Stations 2 and 4 through 8) to reduce raw material losses and waste treatment costs.

Alkaline Rinse (Station 2) and Pickling Rinse (Station 4): Testing indicated that with air agitation the rinse rate for each station could be reduced from 360 to 180 gal/h (1,363 to 681 l/h) with adequate rinsing efficiency. This reduction was accomplished by installing a venturi-style water flow regulator that also provided air agitation. In addition, the overflow from the acid rinse was fed to a suction pump and was used as the feed to the alkaline rinse. Combined, these modifications reduced process water demand at these two stations from 720 to 180 gal/h (2,725 to 680 l/h).

Costs for the modifications came to $2,000; this total consisted of:

- Pump and foundation, $1,300
- Flow regulators, piping, valves, and electrical connections, $300
- Labor, $400

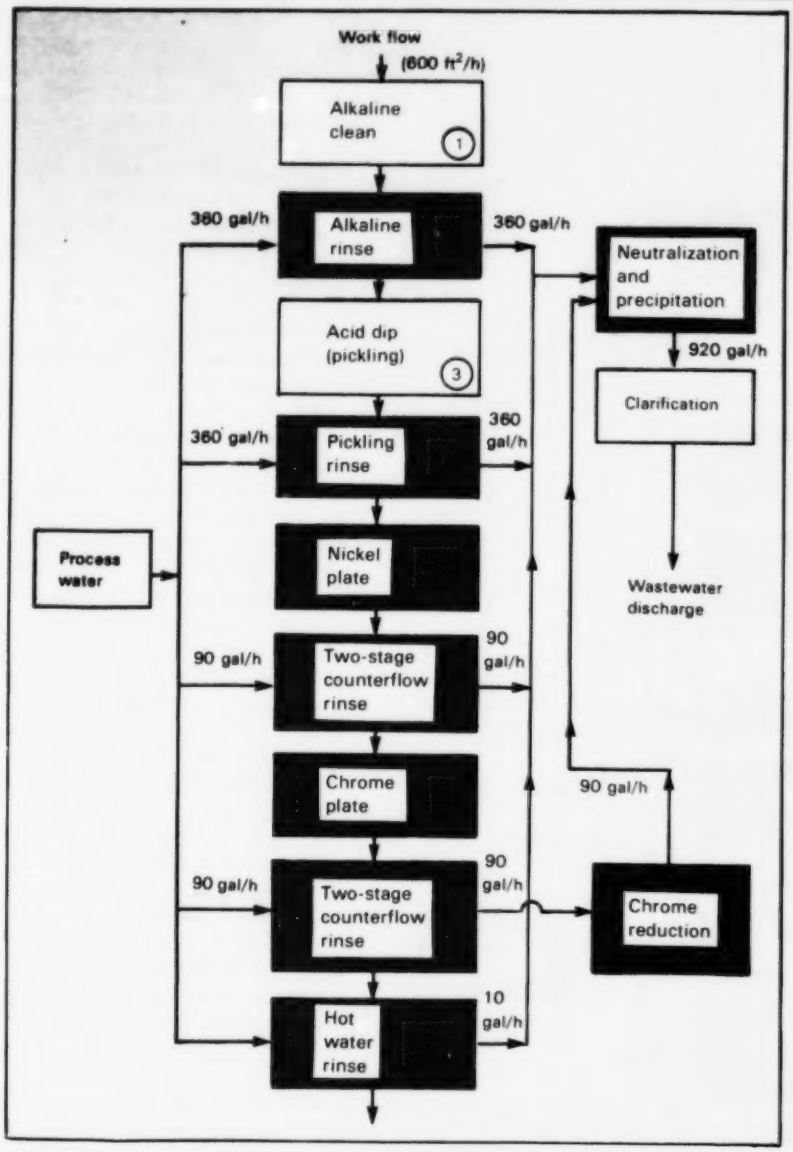


Figure 35.

Nickel-Chrome Plate Sequence and Waste Flow Rates

Nickel Plate and Rinse (Stations 5 and 6): The nickel plating bath operates at 150° F (66° C) and has the following chemical composition:

- $NiSO_4 \cdot 6H_2O$ = 45 oz/gal (337 g/l); $NiSO_4$ = 1.65 lb/gal (0.2 kg/l)
- $NiCl_2 \cdot 6H_2O$ = 10 oz/gal (75 g/l); $NiCl_2$ = 0.34 lb/gal (0.04 kg/l)
- H_3BO_3 = 6 oz/gal (45 g/l), or 0.38 lb/gal (0.045 kg/l)
- Specific gravity = 1.25

The plate tank has a surface area of 30 ft² (2.8 m²) and drag-out is determined by testing to equal 1.5 gal/1,000 ft² (61 l/1,000 m²) of work plated, or at 600 ft²/h (56 m²/h) plated, 0.9 gal/h (3.4 l/h) drag-out. The tank is aerated at a rate of 60 stdft³/min (1.7 normal m³/min). From Figure 28, the evaporative rate in the plating tank will be 5.85 gal/h (22.14 l/h).

The plant decided to reduce drag-out losses by employing a rinse-and-recycle system similar to that in Figure 31. By use of the existing two-stage, countercurrent rinse as a single-stage recovery rinse and a single-stage final rinse, drag-out losses can be reduced by 85 percent—from Figure 29 based on a recovery rinse ratio of (5.85 gal/h)/(0.9 gal/h) = 6.5. If an additional rinse tank were installed, and a two-stage recovery rinse were operated before the single-stage final rinse, the recovery system would reclaim 98 percent of the current drag-out losses. An evaluation of whether to add an additional rinse tank was performed. Table 12 summarizes the results. Case 1 represents the current operating practice. Case 2 represents a rinse and recycle system using the two existing rinse tanks. Case 3 represents adding an additional rinse tank and operating a two-stage recovery rinse.

The additional $3,000 investment for a third rinse tank further reduced operating costs by $2,545 per year (Case 3). Because of this excellent return on investment, Case 3 was chosen.

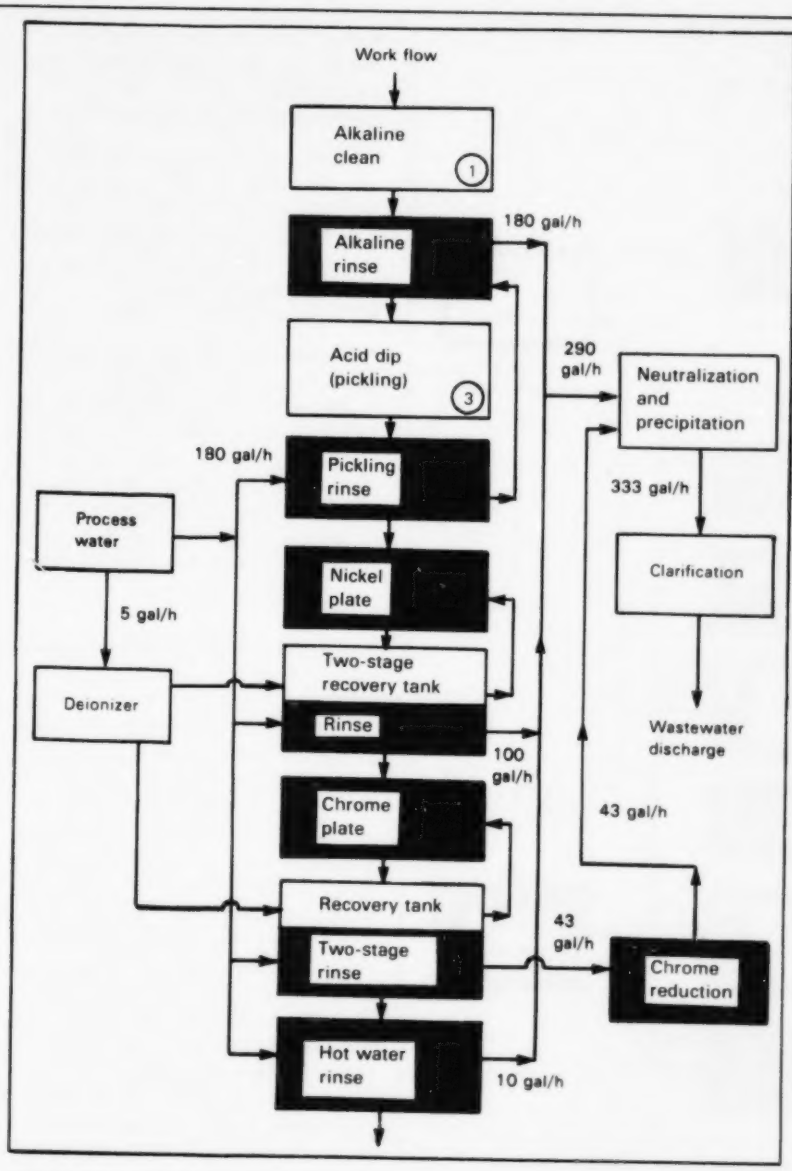


Figure 36.

Nickel-Chrome Plate Sequence with Wastewater Flow Rates Revised

Chrome Plate and Rinse (Stations 7 and 8): The plating tank has a surface area of 30 ft^2 (2.8 m^2) and drag-out averages 1.5 gal/1,000 ft^2 (61 l/1,000 m^2) of work plated, or at 600 ft^2/h (56 m^2/h) plated, 0.9 gal/h (3.4 l/h) drag-out. This tank is also aerated at a rate of 60 $stdft^3$/min (1.7 m^3/min). The plating solution contains 50 oz/gal (375 g/l), or 3.125 lb/gal (0.375 kg/l), chromic acid (H_2CrO_4), has a specific gravity of 1.25, and is maintained at 120° F (49° C). From Figure 28 surface evaporation rate is 2.4 gal/h (9.1 l/h).

A rinse-and-recycle system, as shown in Figure 31, would operate at a rinse ratio of (2.4 gal/h)/(0.9 gal/h) = 2.66. If an additional rinse tank were installed and a two-stage recovery rinse were operated, 90 percent of the drag-out would be recycled (Figure 32). A one-stage recovery rinse could recover 72 percent of the current losses. The plant decided to add a third rinse tank and an analysis was performed to determine whether it would be more advantageous to operate the three rinse tanks as a two-stage recovery rinse followed by a single-stage final rinse or as a single-stage recovery rinse followed by a two-stage final rinse. Table 13 summarizes the results. Case 1 represents the current operating practice. Case 2 represents the case with a two-stage final rinse. Case 3 is the option using a two-stage recovery rinse.

The two investment options (Cases 2 and 3) require equal capital and reduce operating costs by almost equal amounts; however, Case 3 would result in a tenfold increase in wastewater flow to the chromium reduction waste treatment system: 81 gal/h vs. 730 gal/h (307 l/h vs. 2,763 l/h). This volume increase would exceed the capacity of the unit and would reduce the efficiency of downstream waste treatment equipment. When the additional criteria were considered, Case 2 represented the most attractive option and these modifications were incorporated into the plating sequence.

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Table 12.
Nickel Plate Cost Reduction Evaluation of Rinsing Options

Table 13.
Chrome Plate Cost Reduction Evaluation of Rinsing Options

Item	Case 1 (present 2-stage rinse)	Case 2 (proposed 1-stage recovery rinse, 2-stage final rinse)	Case 3 (proposed 2-stage recovery rinse, 1-stage final rinse)
Required modifications	—	Level control rinse feed, conductivity controller, repiping, additional rinse tank	Level control rinse feed, conductivity controller, repiping, additional rinse tank
Cost of modifications	—	$5,500	$5,500
Drag-out recovery	0	72%	90%
Drag-out losses[a]	$13,300/yr	$3,720/yr	$1,330/yr
Rinse water required[b]	81 gal/h	43 gal/h	730 gal/h
Water use cost (at $1.10/1,000 gal)	$270	$140	$2,410
Annual operating cost[c]	$13,570	$4,410	$4,290
Annual savings	—	$9,160	$9,280

[a]See Table 10.

[b]From Figure 27, C_n = 37 mg/l.

[c]Depreciation at 10-year straight line.

Summary of Savings. The total cost of the modifications described was $12,500. The cost assumes that the plate baths already have purification systems that would control any contaminant buildup resulting from recycling the drag-out back to the baths. The benefits from the modifications include:

- The cost to operate the nickel plating bath is reduced by $5,100 per year.
- The cost to operate the chrome plating bath is reduced by $9,300 per year.
- The baseline flow to waste treatment is reduced from 910 gal/h to 330 gal/h (3,445 to 1,250 l/h) (Figure 29). The plater is now ensured of having a discharge rate of less than 10,000 gal/d (37,854 l/d), putting the plater in an industry category with different treatment regulations in the proposed pretreatment standards.
- Because the waste treatment process reduces the solubility of pollutants to an equilibrium level, the quantity of pollutants discharged in the wastewater effluent is reduced to the same degree as the volume of effluent.

5. Recovery Processes

Introduction

The high cost of replacing and treating plating chemicals lost to the waste stream has resulted in the application of various separation processes to reclaim these materials for reuse. These processes all operate on the same basic principle; they concentrate the dragged-out plating solution contained in the rinse water to the degree that the solution can be returned to the plating bath.

Recovery processes include evaporation, reverse osmosis, ion exchange, and, most recently, electrodialysis. Their use can result in an essentially closed system around a plating bath; no plating chemicals are consumed other than those plated on the ware, and no rinse water is sent to waste treatment. Except in the case of purge streams from the recovery unit, under very favorable conditions a recovery system (Figure 37a) can achieve zero effluent discharge.

Using a recovery unit requires reducing the volume of rinse water to a quantity that can be processed economically. The use of a multistage counterflow rinse system is therefore recommended. A bath purification system is needed to eliminate the buildup of contaminants in the closed-loop system resulting from return of the drag-out to the process bath. The drag-out formerly acted as a bleed stream and served to control the buildup of contaminants. The type of purification system required depends on the type of plating chemicals being recovered.

One objection to recovery systems is that the quality of the rinse operation may be compromised. Rinsing quality can be ensured by segregating the final rinse from the recovery process (Figure 37b), but this approach results in a rinse water flow to waste treatment.

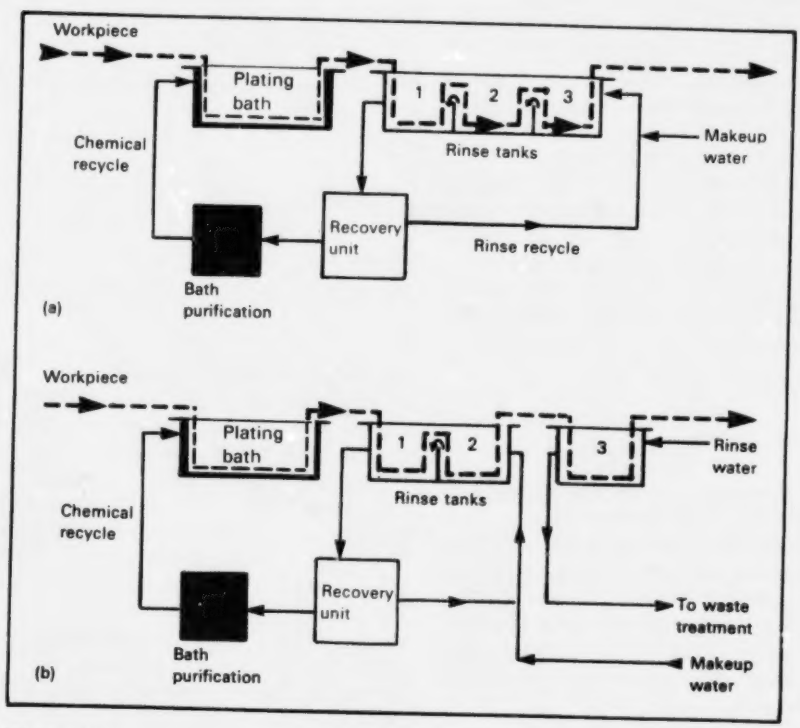


Figure 37.

Recovery Systems: (a) Closed Loop; (b) Open Loop

The chemical recovery potential for a recovery system is shown as a function of rinse ratio in Figure 38. The curve is the same as that developed for the recovery potential of a two-stage rinse-and-recycle system in Figure 32. The major difference is that now the recovery rinse ratio is determined by the processing capability of the recovery unit, not the surface evaporation rate of the plating bath. Recovery processes should be considered for those baths for which rinse-and-recycle modifications are not applicable. If a plater can reclaim 90 percent of his drag-out losses by low-cost modifications to the plate line, as realized by the nickel system described in Section 4, then it would not be economical to install a recovery system.

In cases where the rinse waters following a plating operation require a separate waste treatment system (chromium and cyanide are examples), closing the loop around the plating operation with a recovery system can avert the need for the treatment system. The capital savings resulting from eliminating the treatment hardware will make the investment in recovery units more attractive.

This section will examine the operating parameters, cost factors, and reliability of the different recovery systems used in the electroplating industry. This information will enable the electroplater, after an assessment of specific loss factors, to determine the economy that could be realized by installing recovery units.

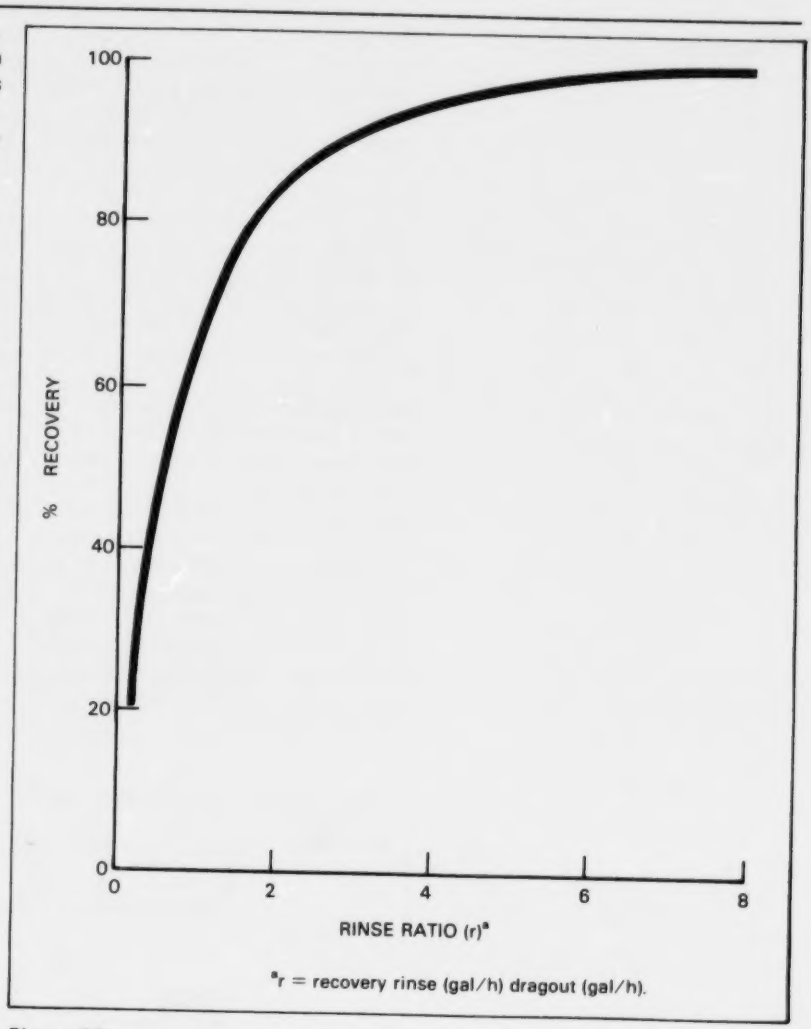


Figure 38.

Recovery Potential for a Two-Stage Counterflow Rinse

Evaporation

Evaporation was the first separation process used to recover plating chemicals lost to rinse streams. The process has been demonstrated successfully on virtually all types of plating baths, and currently several hundred units are being operated to reclaim plating solutions from rinse streams.

Recovery is accomplished by boiling off sufficient water from the collected rinse stream to allow the concentrate to be returned to the plating bath. The condensed steam is recycled for use as rinse water in the rinse tanks. The boil-off rate, or evaporator duty, is set to maintain the water balance of the plating bath. The evaporation usually is performed under a vacuum to prevent any thermal degradation of additives in the plating solution and to reduce the amount of energy consumed by the process.

Figure 39 diagrams a closed-loop evaporative recovery system used on a chromium plating bath with a three-stage, countercurrent rinse system. No losses in plating chemicals occur. Only the chromium plated on the wares must be added to the plating tank. Water consumption is reduced to the water lost to surface evaporation. A cation exchange column is required to prevent the buildup of metallic impurities—mainly dissolved metals from the work processed and excess trivalent chromium—in the closed-loop system.

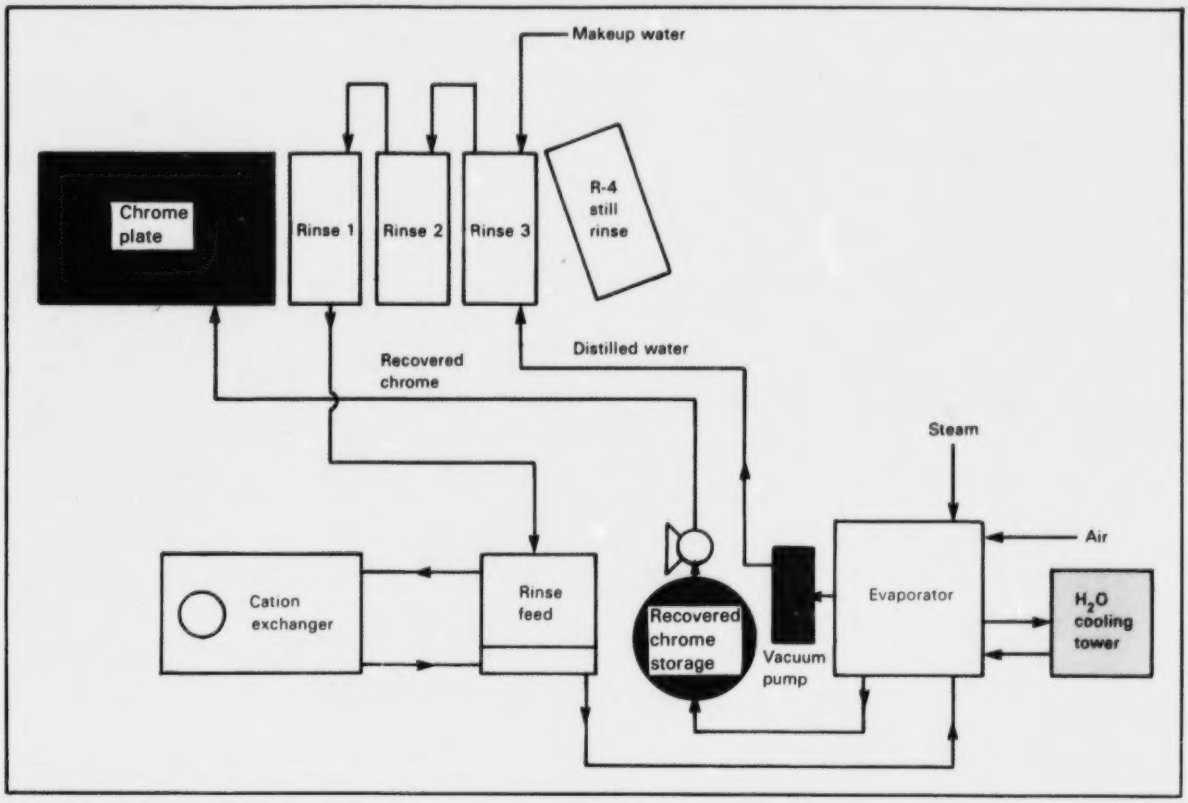


Figure 39.

Chromic Acid Evaporative Recovery Unit

Total installed investment, operating costs, and economics for installing a 20-gal/h (76 l/h) evaporator (as shown in Figure 39) are given in Table 14. The before tax annual savings for this system is approximately $1,800. The cost for steam and fixed charges are the major costs of operation, approximately 55 percent of the total costs. The annual savings resulting from recovery of plating chemicals and wastewater treatment cost reduction comes to $14,880.

The steam costs and investment for evaporators depend on the evaporative duty, which for plating rinse recovery systems is equal to the required rinse water flow rate (Figure 40). To minimize rinse rates, such methods as countercurrent rinse systems are usually cost effective. A 50-percent steam saving can be achieved with double-effect evaporators; however, the capital costs are much higher and operation is more complicated. As a rule, at evaporation rates below 150 gal/h, (568 l/h), additional investment for double-effect evaporators is not justified.

Because of the high initial investment, the savings and economics for evaporative recovery depend to a great extent on the concentration of the rinse water being evaporated and the volume of drag-out. For example, if the 20-gal/h (76-l/h) evaporator (Table 14) were fed a stream with 50 percent more plating chemicals, the annual savings for treatment and recovery would increase by 50 percent to approximately $22,300 (14,880 × 1.5). The net savings would increase to $9,100, and the payback period would reduce to 4.3 years.

Table 14.

Economics of Evaporator System for Chromic Acid Recovery, Operating 5,000 h/yr

Item	Cost
Installed cost, 20-gal/h evaporator ($):	
Equipment:	
Evaporator	19,000
Tanks	1,660
Pumps	750
Cation exchanger	6,200
Piping	2,500
Miscellaneous	450
Subtotal	30,560
Installation, labor and materials:	
Site preparation	280
Plumbing	2,660
Electrical	1,230
Equipment erection	270
Miscellaneous	500
Subtotal	5,120
Total installed cost	35,680
Annual operating cost ($/yr):	
Labor, 100 h/yr at $7/h	700
Supervision	(*)
Maintenance, 6% of investment	2,190
General plant overhead	660
Raw materials, cation exchanger:	
H_2SO_4, 3,500 lb/yr at $0.028/lb	100
NaOH, 3,000 lb/yr at $0.08/lb	240
Utilities:	
Electricity, $0.045/kWh	1,400
Cooling water, 1,000 gal/h × $0.10/1,000 gal	500
Steam, $3.00/$10^6$ Btu	3,150
Total operating cost	9,160
Annual fixed costs ($/yr):	
Depreciation, 10% of investment	3,570
Taxes and insurances, 1% of investment	360
Total fixed costs	3,930
Total costs of operation	13,090
Annual savings ($/yr):	
Recovered plating chemicals, (1.875 lb/h H_2CrO_4	7,310
Water treatment chemicals	4,500
Sludge disposal	3,000
Water use, 13 gal/h at 1.10/1,000 gal	70
Total annual savings	14,880
Net savings = annual savings − (operating cost + fixed cost) ($/yr)	1,790
Net savings after taxes, 48% tax rate ($/yr)	930
Average ROI = (net savings after taxes/total investment) X 100 (%)	2.6
Cash flow from investment = net savings after taxes + depreciation ($/yr)	4,500
Payback period = total investment/cash flow (yr)	7.9

*None required.

[illegible] Table 15, based on a 90% operating factor.

Note.—If the evaporator installation had eliminated the need for a chromium reduction system, a $17,000 investment in treatment equipment would have been required. In this case, the additional investment for the evaporator would have an after-tax average ROI of 10.2%, and the payback period would be 5.9 yr.

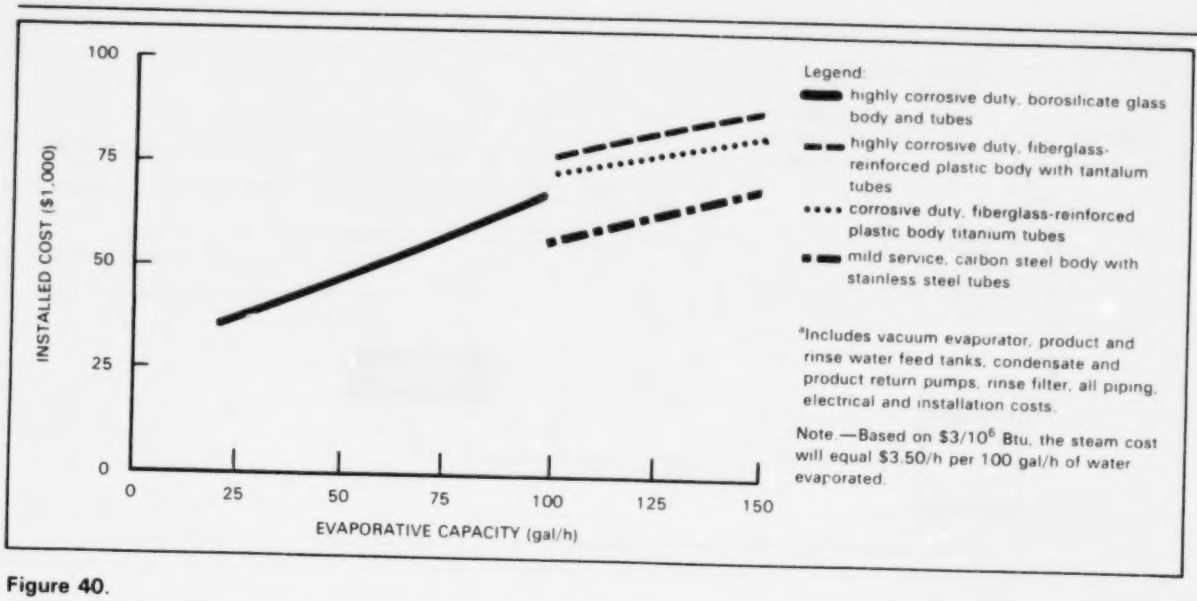

INSTALLED COST ($1,000)
100
75
50
25
0
0
25
50
75
100
125
150
EVAPORATIVE CAPACITY (gal/h)
Legend:
highly corrosive duty, borosilicate glass body and tubes
highly corrosive duty, fiberglass-reinforced plastic body with tantalum tubes
corrosive duty, fiberglass-reinforced plastic body titanium tubes
mild service, carbon steel body with stainless steel tubes
[a]Includes vacuum evaporator, product and rinse water feed tanks, condensate and product return pumps, rinse filter, all piping, electrical and installation costs.
Note.—Based on $3/10^6$ Btu, the steam cost will equal $3.50/h per 100 gal/h of water evaporated.

Figure 40.

Installed Costs and Energy Costs for Evaporative Recovery Systems

If the concentration of the plating chemicals shown in Table 14 were to remain constant, but the volume of drag-out were to double, a 40-gal/h (151-l/h) evaporator would be required. As Figure 40 shows, the installed cost would be approximately $45,000. Because the installed cost increased by only $9,000, the net annual savings would be $10,300, which yields a payback period of 4.6 years after taxes.

Reverse Osmosis

Reverse osmosis (RO) (Figure 41) is a pressure drive membrane separation process. The feed is separated under pressure—400 to 800 lb/in^2 gauge—into a purified "permeate" stream and a concentrate stream by selective passage of water through the microscopic pores of the semipermeable membrane. Commercial RO units have been successful in concentrating and recycling rinse streams in metal plating operations for a number of years. The main area of application is the concentration of rinse waters from acid nickel plating baths.

The major limitation of commercial RO systems is the inability to maintain membrane performance. Fouling and gradual deterioration of membranes can reduce the processing capacity of the unit and require frequent membrane replacements. Currently feed solutions must be in a pH range between 2.5 and 11 to ensure reasonable life for commercially available membranes.

Moreover, these membranes are not suitable for treating solutions having a high oxidation potential. RO units have limited capability for high concentration of dilute feed solutions. Table 15 lists typical maximum concentrations reached in commercial applications. Because of these concentration limits, additional concentration by a small evaporator may be required for ambient temperature baths where there is minimum surface evaporation. Therefore, acid nickel plating baths, which have considerable surface evaporation, are the primary area of application for RO.

Furthermore, the membrane does not completely reject certain species, such as non-ionized organic wetting agents. This limitation necessitates more frequent bath analysis to maintain the desired chemical makeup of the plating bath.

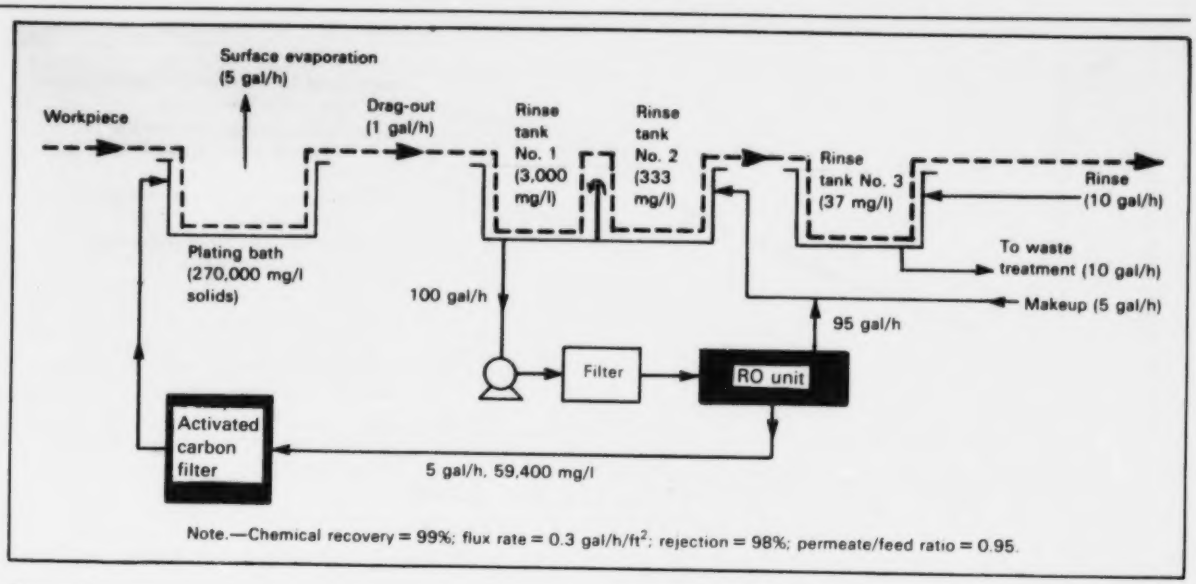


Figure 41.

Reverse Osmosis for Nickel Plating Drag-Out Recovery

Table 15.

Reverse Osmosis Operating Parameters

Feed solution	Maximum concentration of concentrate (%)	Rejection (%)
Ni^{+2}	10-20	98-99
Cu^{+2}	10-20	98-99
Cd^{+2}	10-20	96-98
CrO_4^{-2}[a]	10-12	90-98
CN^{-}[a]	4-12	90-95
Zn^{+2}	10-20	98-99
Low molecular weight organics	([b])	([b])

[a]Performance depends greatly on pH of solution.

[b]These compounds are concentrated in permeate stream because of selective passage through membrane.

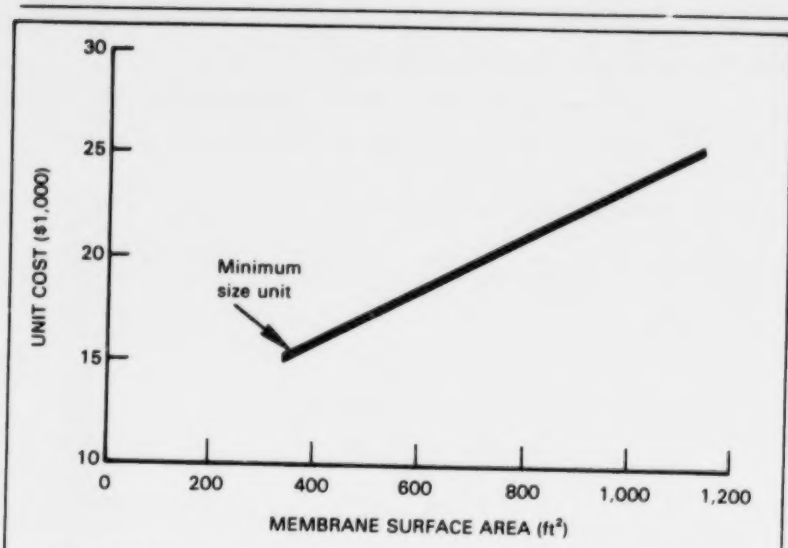
The performance of RO units is defined by flux—the rate of passage of purified rinse water through the membrane per unit of surface area—and the percent rejection of a dissolved constituents in the rinse water, which relates to the membrane's ability to restrict that constituent from entering the permeate stream. Percent rejection is defined by:

$$\text{Percent rejection} = \frac{C_f - C_p}{C_f} \times 100$$

where

C_f = concentration in feed stream
C_p = concentration in permeate stream

Figure 42 presents the cost of RO units as a function of membrane surface area. Determination of the flux rates for a specific application, and thus the membrane surface area necessary, usually requires testing by the vendor. As an approximate tool, the flux rate of 0.3 gal/h/ft² (12.2 l/h/m²)—indicated in Figure 41 for a nickel plating bath with a feed concentration of 3,000 mg/l and a permeate/feed ratio of 0.95—can be used to determine membrane surface area requirements.



Note.—Unit includes feed pump, filter and membrane modules, preassembled, requiring only utility connections.

Figure 42.

Reverse Osmosis System: Unit Cost vs. Membrane Surface Cost

The flux rate will decrease as the feed concentration increases. Higher permeate/feed ratios also will decrease the flux rate. Experience has shown that doubling the feed concentration or reducing the concentrate volume by 50 percent (increasing the permeate/feed ratio from 0.95 to 0.975) will decrease the flux rate by 25 percent. For example, if the RO system shown in Figure 41 were to concentrate the drag-out into 2.5 gal/h (9.5 l/h) of concentrate instead of the 5 gal/h (19 l/h) shown, the membrane surface area requirements would increase from 317 to 422 ft^2 (29.5 to 39.2 m^2).

The RO system shown in Figure 41 is used to recycle the chemical drag-out in an acid nickel plating operation. The system uses a 50-μm filter to prevent blinding of the membrane by solid particles. The preassembled RO unit consists of a high pressure centrifugal pump and six membrane modules, and installation requires only piping and electrical connections. An activated carbon filter is used to avoid organic contaminant buildup in the plating bath.

The cost of the system, itemized in Table 16, comes to $19,500. Theoretically, the system would recover 99 percent of the plating chemicals lost to the rinse system. Table 16 also presents the operating cost reduction that would be achieved if the unit operated 90 percent of the time. The system has a payback period of 4.3 years.

Table 16.

Economics of Reverse Osmosis System for Nickel Salt Recovery, Operating 5,000 h/yr

Item	Cost
Installed cost, 330-ft^2 unit ($):	
Equipment:	
RO module including 50-μm filter, pump, and 6 membrane modules at 55 ft^2 per module	15,000
Activated carbon filter	2,000
Piping	500
Miscellaneous	500
Subtotal	18,000
Installation, labor and material:	
Site preparation	200
Plumbing	300
Electrical	500
Miscellaneous	500
Subtotal	1,500
Total installed cost	19,500
Annual operating cost ($/yr):	
Labor, 100 h/yr at $7.00/h	700
Supervision	([a])
Maintenance	1,170
General plant overhead	660
Raw materials:	
Module replacement, 2-yr life (6 × $320)/(module × 0.5 yr)	960
Resin for carbon filter	500
Utilities, electricity (0.045/kWh)	510
Total operating cost	4,500
Annual fixed costs ($/yr):	
Depreciation, 10% of investment	1,950
Taxes and insurance, 1% of investment	200
Total fixed costs	2,150
Total cost of operation	6,650
Annual savings ($/yr):[b]	
Plating chemicals:	
1.65 lb/h $NiSO_4$	5,640
0.34 lb/h $NiCl_2$	1,590
Water treatment chemicals	2,520
Sludge disposal cost	1,810
Water use (no saving)	—
Total annual savings	11,560
Net savings = annual savings − (operating cost + fixed cost) ($/yr)	4,910
Net savings after taxes, 48% tax rate, 4,915 × 0.52 ($/yr)	2,550
Average ROI = (net savings after taxes/total investment) × 100 (%)	13
Cash flow from investment = net savings after taxes + depreciation ($/yr)	4,500
Payback period = total investment/cash flow (yr)	4.3

[a]None required.

[b]From Table 10, based on a 90% operating factor.

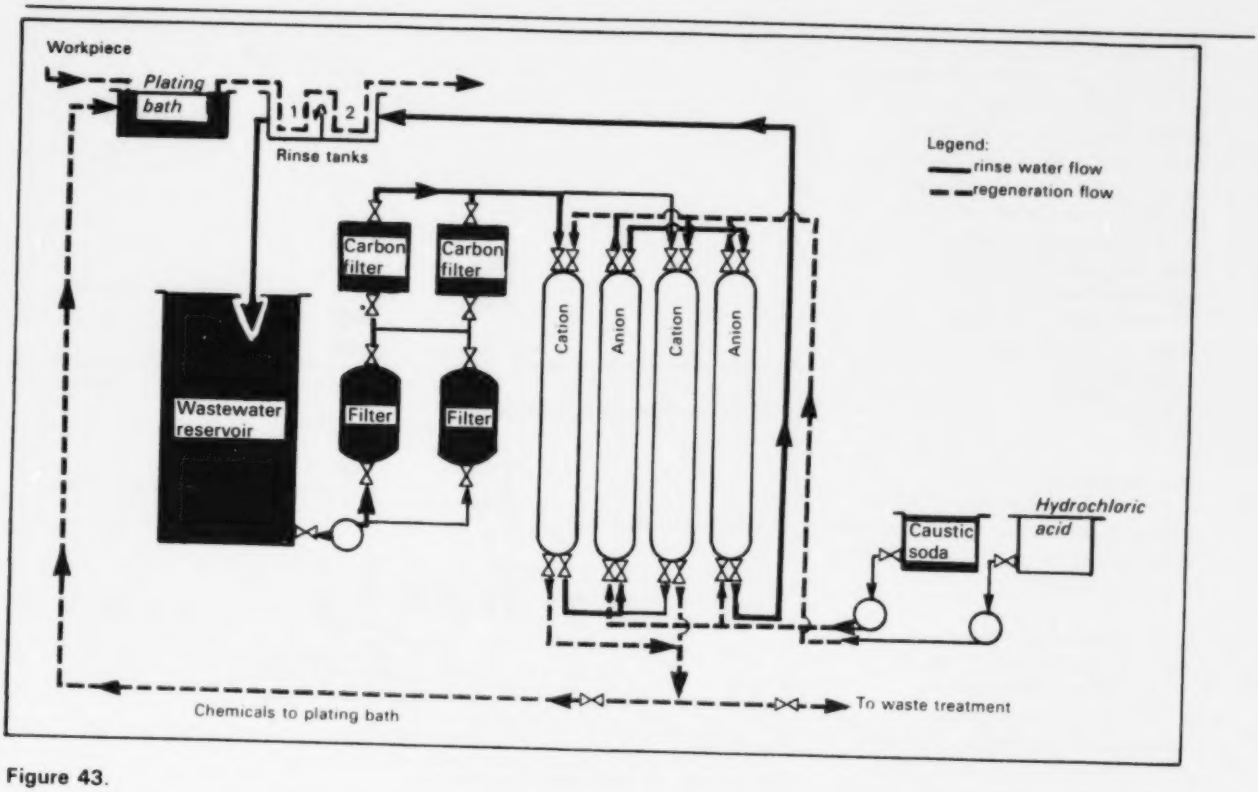


Figure 43.

Fixed-Bed Ion Exchanger System for Chromic Acid Recovery

Ion Exchange

In ion exchange, a chemical solution is passed through a bed of resin, which selectively removes either the positively charged cations (e.g., Cu^{+2}, Fe^{+2}) or the negatively charged anions (e.g., CrO_4^{-2}, CN^-) from the solution. This removal is accomplished by the exchange of an ion[b] from the surface of a resin particle for a similarly charged ion in the solution. Ion exchange is used in the electroplating industry to remove trace pollutants from wastewater after a conventional treatment process, or to recover plating solution drag-out from rinse water and to return the purified water for reuse.

Unlike other recovery systems, the economics of which are inversely proportional to the chemical concentration, ion exchange is ideally suited for dilute solutions. The treated water is of high purity.

A major drawback of ion exchange is that the resin must be regenerated after it has exhausted its exchange capacity. This problem complicates the operation of the system considerably and results in small volumes of wash solution, which adds to the waste treatment loading.

Figure 43 is a fixed-bed ion exchange system used to recover chromic acid from rinse waters. Initially, water would pass in series through a cation column and two anion columns. The cation column is used to remove any heavy metal contaminants. The anion columns remove the hexavalent chromium from the rinse water. When the upstream anion column has exhausted its exchange sites, it is taken off stream and regenerated with a caustic solution. This column is then returned to service as the downstream anion column.

[b]An ion is a charged molecule; it is a cation if its charge is positive, an anion if its charge is negative.

The product of the anion column regeneration is sodium chromate and any excess caustic used; it would be passed directly to a second cation column where the sodium ions would be exchanged for hydrogen ions, yielding chromic acid and water. This solution can be returned to the plating bath. Both cation columns are regenerated with an acid solution when saturated. The spent regeneration solutions must be treated in the neutralizer for pH adjustment and precipitation of dissolved heavy metals.

Two approaches have been used to simplify the operation of ion exchange systems: the continuous ion exchange column and the reciprocating flow ion exchanger.

The continuous ion exchange column (Figure 44) is a closed loop of connected vessels providing simultaneous ion exchange, regeneration, back wash, and rinse cycles in separate sections. This design eliminates the need for multiple columns and regeneration labor. It also uses regeneration chemicals more efficiently. The unit's automation, however, makes its capital cost higher than fixed-bed units and feasible only for large volume treatment systems.

The reciprocating flow ion exchanger (Figure 45) was especially developed for purifying the bleed stream of a large-volume solution, such as the rinse overflow from an electroplater's rinse tank. This unit operates on the principle that for the short period of time the unit goes off stream for regeneration, the buildup of contaminants in the rinse system is negligible. Capital costs are significantly lower for units of this design than for fixed-bed units. Moreover, because the units are automated, they require only minimum operator attention.

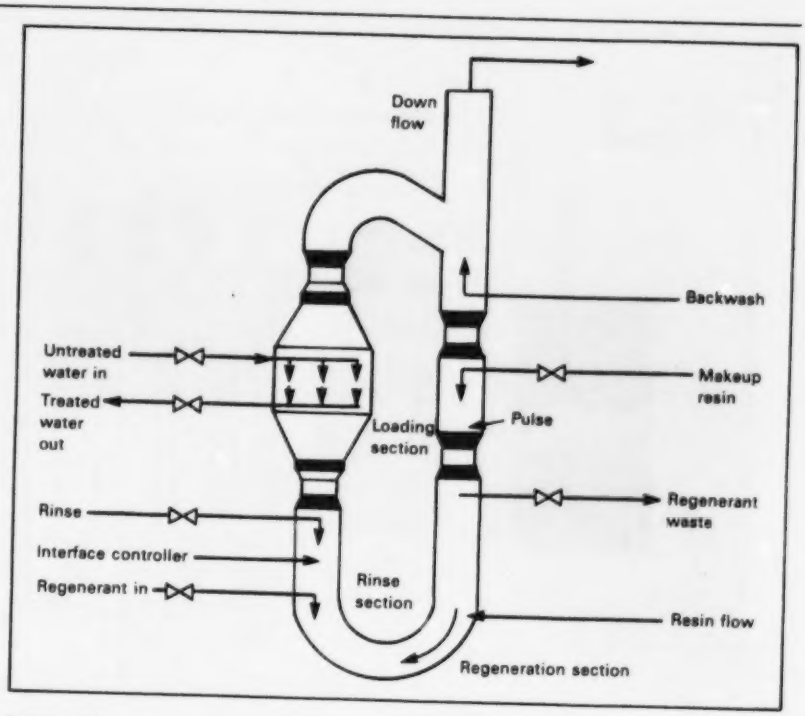


Figure 44.

Continuous Ion Exchange System

Several reciprocating units with various column configurations are being used to reclaim plating chemicals from rinse streams and for removing metal impurities from various acid baths. The reciprocating flow exchanger has been marketed for only 3 years, and its long-term durability and reliability are not established.

The reciprocating flow ion exchanger enjoys a significant capital cost advantage compared with the fixed-bed system in plating chemical recovery applications, primarily because it requires exchanger columns only a fraction the size of the columns required for the fixed-bed system. Furthermore, the unit regenerates itself and requires less operator attention. Table 17 presents the total installed investment, operating costs, and cost benefits of installing a reciprocating flow ion exchanger to recover drag-out from a chromium plating operation.

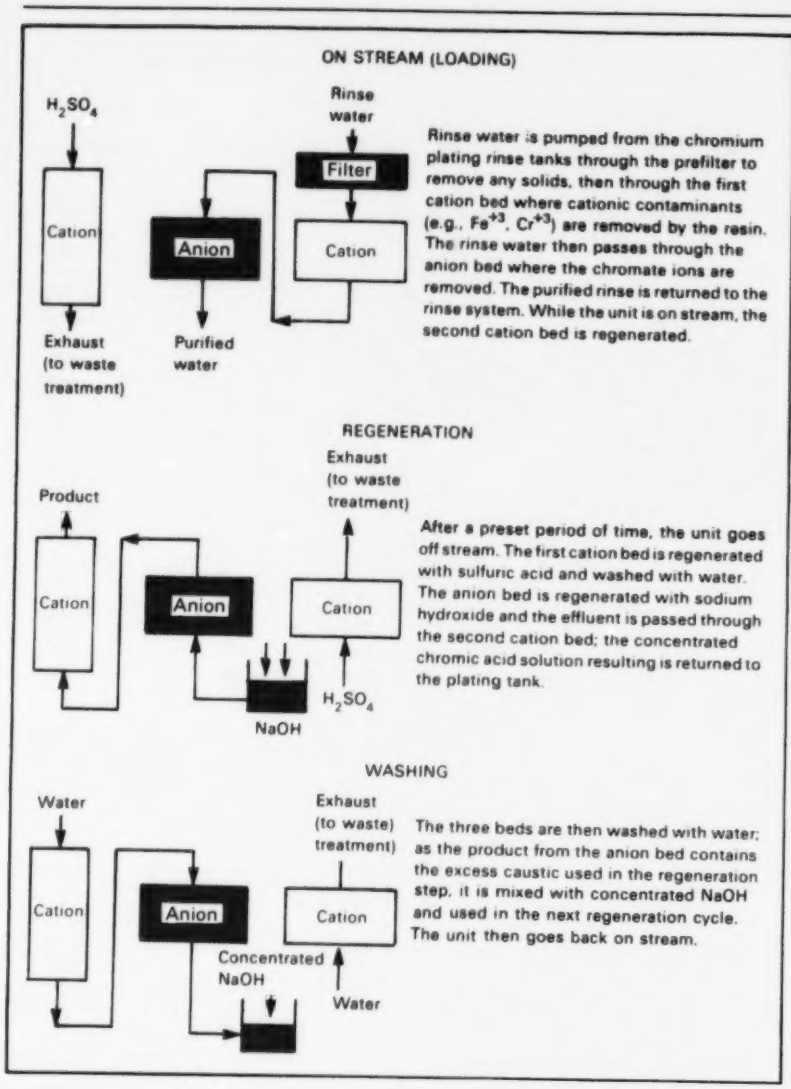

ON STREAM (LOADING)
H_2SO_4
Rinse water
Filter
Cation
Anion
Cation
Exhaust (to waste treatment)
Purified water
Rinse water is pumped from the chromium plating rinse tanks through the prefilter to remove any solids, then through the first cation bed where cationic contaminants (e.g., Fe^{+3}, Cr^{+3}) are removed by the resin. The rinse water then passes through the anion bed where the chromate ions are removed. The purified rinse is returned to the rinse system. While the unit is on stream, the second cation bed is regenerated.
REGENERATION
Product
Exhaust (to waste treatment)
Cation
Anion
Cation
H_2SO_4
NaOH
After a preset period of time, the unit goes off stream. The first cation bed is regenerated with sulfuric acid and washed with water. The anion bed is regenerated with sodium hydroxide and the effluent is passed through the second cation bed; the concentrated chromic acid solution resulting is returned to the plating tank.
WASHING
Water
Exhaust (to waste) treatment)
Cation
Anion
Cation
Concentrated NaOH
Water
The three beds are then washed with water; as the product from the anion bed contains the excess caustic used in the regeneration step, it is mixed with concentrated NaOH and used in the next regeneration cycle. The unit then goes back on stream.

Figure 45.

Reciprocating Flow Ion Exchanger Operating Cycle

Electrodialysis

Electrodialysis (Figure 46) concentrates or separates ionic species contained in a water solution. The process is well established for purifying brackish water, and recently has been demonstrated for recovery of metal salts from plating rinse. Compact units suitable for this application have been recovering metal values successfully from rinse streams for approximately 3 years. In addition, a recent EPA demonstration project confirmed the applicability of electrodialysis for recovery of plating solutions.

In electrodialysis, a water solution is passed through alternately placed cation permeable and anion permeable membranes. An electrical potential is applied across the membrane to provide the motive force for the ion migration. Essentially, these ion selective membranes are thin sheets of ion exchange resin reinforced by a synthetic fiber backing.

Table 17.

Economics of Reciprocating Flow Ion Exchange System for Chromic Acid Recovery, Operating 5,000 h/yr

Item	Cost
Installed cost ($):	
Equipment:	
Reciprocating flow ion exchanger, including cartridge filter and three ion exchanger beds	28,500
Piping	500
Miscellaneous	500
Subtotal	29,500
Installation, labor and material:	
Site preparation	200
Plumbing	300
Electrical	500
Miscellaneous	500
Subtotal	1,500
Total installed cost	31,000
Annual operating cost ($/yr):	
Labor, 100 h/yr at $7.00/h	700
Supervision	([a])
Maintenance	1,860
General plant overhead	800
Raw materials:	
Replacement resin	500
Regeneration chemicals:	
NaOH	680
H_2SO_4	670
Utilities, compressed air	200
Total operating cost	5,410
Annual fixed costs ($/yr):	
Depreciation, 10% of investment	3,100
Taxes and insurance, 1% of investment	310
Total fixed cost	3,410
Total cost of operation	8,820
Annual savings ($/yr):[b]	
Plating chemicals, 2 lb/h H_2CrO_4	7,020
Water treatment chemicals	4,320
Sludge disposal	2,880
Water use, 18 gal/h at $1.10/1,000 gal	100
Total annual savings	14,320
Net savings = annual savings − (operating cost + fixed cost) ($/yr)	5,500
Net savings after taxes, 48% tax rate ($/yr)	2,860
Average ROI = (net savings after taxes/total investment) × 100 (%)	9.2
Cash flow from investment = net savings after taxes + depreciation ($/yr)	5,960
Payback period = total investment/cash flow (yr)	5.2

[a]None required.

[b]From Table 10, based on a 90% operating factor.

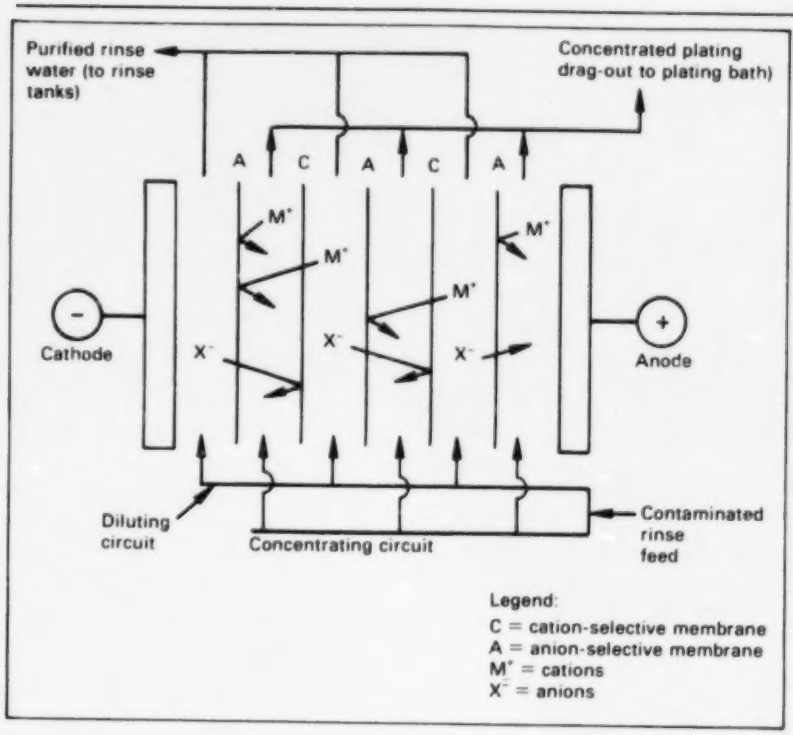


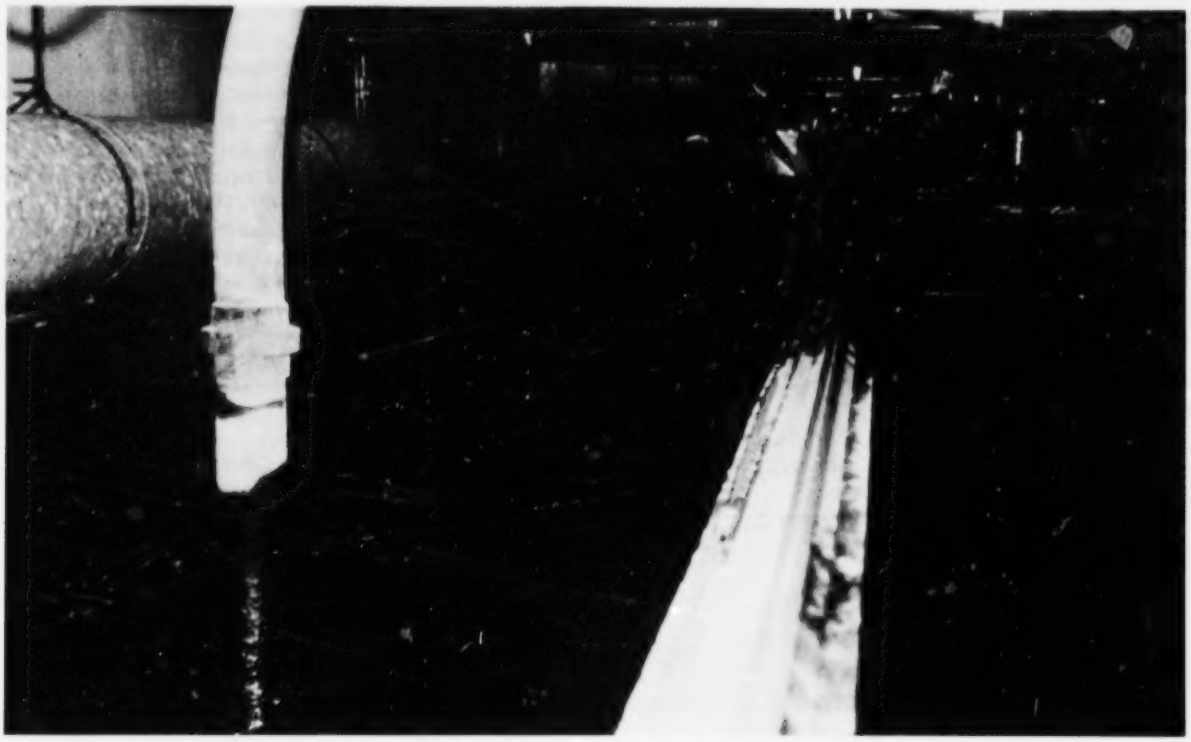
Figure 46.

Electrodialysis Unit Flow Schematic

The flow is directed through the membrane in two hydraulic circuits—one ion depleted, the other ion concentrated. The flow rate through each circuit can be set to achieve the high level of concentration required for returning the plating chemicals to the plating bath. The degree of purification achieved in the diluting circuit is set by the electrical potential passed across the membrane. The ability to pass the charge is proportional to the concentration of ionic species in the dilution stream. Because ion migration is proportional to electrical potential, the optimum system is a trade-off.

The recent EPA demonstration project tested the applicability of an electrodialysis unit to recover nickel from rinse waters for reuse in the plating bath. Operation of the system diagramed in Figure 47 began in September 1975 and continued until June of 1976, with no significant operating problems. Table 18 itemizes the cost of the demonstration unit and the operating advantages attributable to the unit.

Electrodialysis units patterned after the model described are being marketed to reclaim metal values from rinse streams. The units are skid mounted and require only piping and electrical connections. Their cost is approximately $25,000.



Clarifier/thickener with sludge holding tank

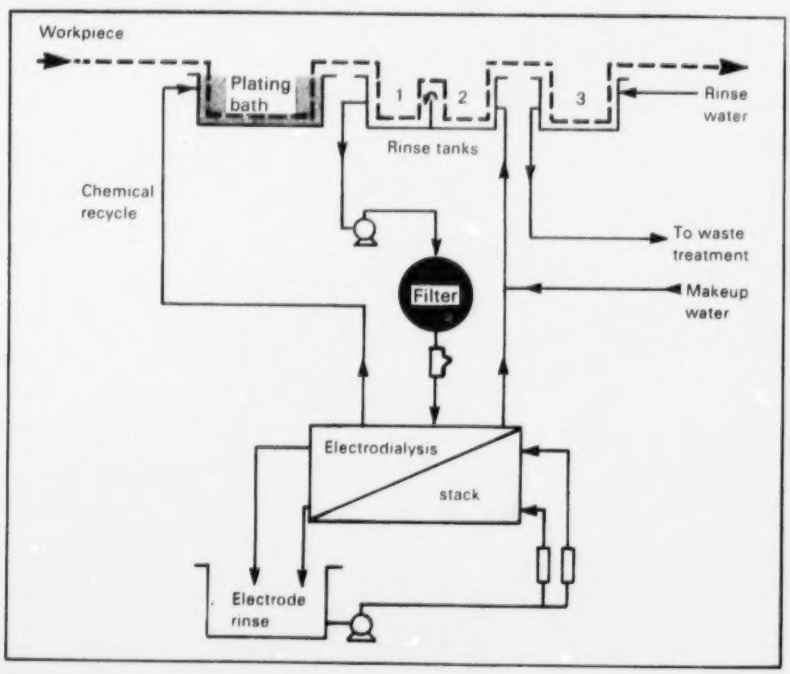


Figure 47.

Electrodialysis Unit for Nickel Plating Drag-Out Recovery

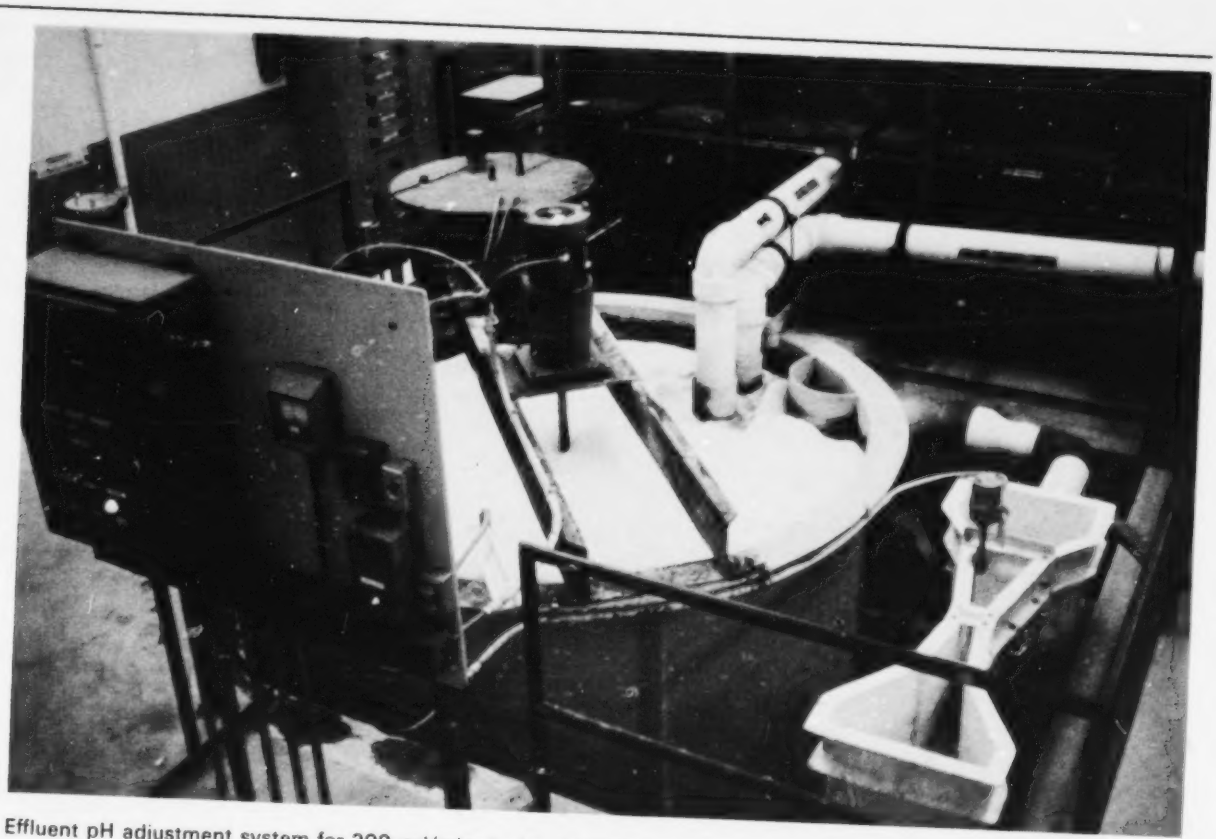
Table 18.

Economics of Electrodialysis System for Nickel Plating Solution Recovery, Operating 5,000 h/yr

Item	Cost
Installed cost ($):	
Equipment:	
Electrodialysis unit, complete with cartridge filter strainer and electrode rinse system	25,000
Piping	500
Miscellaneous	500
Subtotal	26,000
Installation, labor and material:	
Site preparation	200
Plumbing	300
Electrical	500
Miscellaneous	500
Subtotal	1,500
Total installed cost	27,500
Annual operating cost ($/yr):	
Labor, 100 h/yr at $7.00/h	700
Supervisor	([a])
Maintenance	1,650
General plant overhead	750
Raw materials	
Filter cartridges	750
Replacement membranes	300
Utilities, electricity (0.045/kWh)	200
Total operating cost	4,350
Annual fixed costs ($/yr):	
Depreciation, 10% of investment	2,750
Taxes and insurance, 1% of investment	280
Total fixed costs	3,030
Total cost of operation	7,380
Annual savings ($/yr):[b]	
Plating chemicals, 3.8 lb/h $NiSO_4$	13,250
Water treatment chemicals	4,880
Sludge disposal cost	2,960
Water use (no saving)	—
Total annual savings	21,090
Net savings = annual savings − (operating cost + fixed cost) ($/yr)	13,710
Net savings after taxes, 48% tax rate ($/yr)	7,130
Average ROI = (net savings after taxes/total investment) × 100 (%)	26
Cash flow from investment = net savings after taxes + depreciation ($/yr)	9,880
Payback period = total investment/cash flow (yr)	2.8

[a]None required.

[b]From Table 10, based on a 90% operating factor.



Effluent pH adjustment system for 200-gal/min design flowrate

6. EPA's Research and Development Programs

General

Programs to develop pollution control technologies that can reduce the operating and sludge disposal costs for treating metal finishing wastewater are being conducted by the Metals and Inorganic Chemicals Branch of EPA's Industrial Environmental Research Laboratory in Cincinnati, Ohio, in cooperation with industry, vendors, and industrial associations. This section will cover briefly some of these programs.

Donnan Dialysis

Donnan dialysis is a membrane separation process similar to reverse osmosis or electrodialysis (discussed in Section 5). The driving force used in Donnan dialysis is a result of concentration differences across the membrane as opposed to a pressure or electrical potential differential. The wastewater solution containing metal ions (e.g., nickel) passes through the inside of small diameter tubes fabricated from a cation exchange resin. A regenerant solution (e.g., dilute sulfuric acid) that will dissolve the metal ion is passed over the outside of the tubes countercurrent to the waste stream flow. The metal ions migrate through the membrane and concentrate in the acid solution. Tests have shown that the metal ion concentration in the regenerant solution can be increased to over 10 times the original concentration in the waste stream. Donnan dialysis can achieve metal concentration of 1 ppm in the treated water. The regenerant solution can be returned directly to the plating bath.

The advantage of Donnan dialysis over reverse osmosis and electrodialysis is lower energy use. A major disadvantage of the system is that the regenerant solution will slightly acidify the wastewater, and a use for this water must be found if neutralization and discharge of the stream are to be avoided.

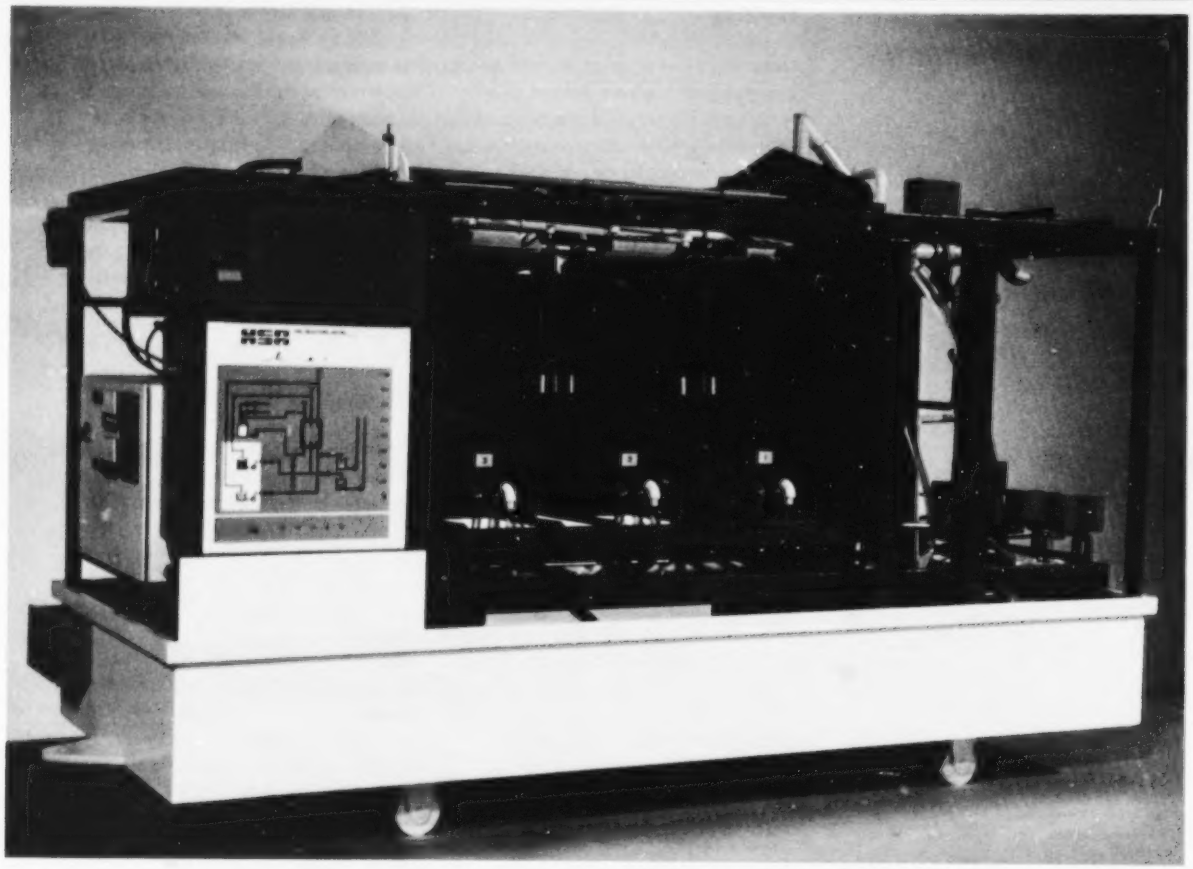
Commercial application of Donnan dialysis to metal recovery or wastewater polishing has been impeded by the lack of a stable ion exchange membrane. A new resin developed by Du Pont may provide a cation exchange membrane of exceptional chemical resistance and good mechanical properties. A full-scale prototype unit employing this membrane is currently being tested for nickel recovery from rinse waters under an EPA grant.

Electrolytic Techniques

Electrolytic techniques can be used to plate out dissolved metals, oxidize cyanide, or reduce chromium from wastewaters. Electrical power needed to supply the current is the major operating cost, and no chemical treatment is required. The major problem is that dilute solutions of electrolytes have a high degree of electrical resistance; consequently, treatment of dilute waste streams becomes prohibitive because of high electricity costs. Recent investigations have, therefore, centered on development of an electrolytic method that could treat dilute solutions and overcome the high electrical resistance of the cell.

Two of the demonstration projects for electrolytic processes nearing commercialization are discussed in the paragraphs that follow.

New England Plating. EPA has cooperated with New England Plating to demonstrate an electrolytic system that employs semiconductive beds of carbon particles to reduce electrical resistance. The full-scale plant designed by Joseph Schockor for New England Plating achieves reduction of chromium and oxidation of cyanide in separate cells. Preliminary economics indicate a cost advantage in this system compared with costs for chemical treatment for chromium concentrations of approximately 150 ppm. Subsequent chemical treatment of the cyanides was required to reach effluent discharge limits.



HSA Electrochemical Reactor on Electroless Nickel

Varland Metal Services. EPA, in cooperation with the Metal Finishing Foundation, is conducting a full-scale demonstration of a carbon fiber electrochemical system that is capable of removal and recovery of heavy metals with simultaneous cyanide oxidation. The system—developed by H.S.A. Reactors, Limited—has been proven successful in recent pilot plant tests. No sludge will result from the process, and concentrated salts can be recycled to the plating baths.

Insoluble Starch Xanthate

Insoluble starch xanthate (ISX) is a new process developed by the U.S. Department of Agriculture and demonstrated in cooperation with EPA. It removes heavy metals from the wastewater to a fraction of 1 ppm. ISX is made from commercial crosslinked starch by reacting it with sodium hydroxide and carbon disulfide. Magnesium sulfate is also added to give the product desired stability and to improve the sludge settling rate. ISX acts as an ion exchange material, removing the heavy metal ions from the wastewater and replacing them with sodium and magnesium.

The treatment process generates a significant amount of sludge (10 pounds of ISX are required to remove 1 pound of copper). The sludge settles rapidly, however, and dewaters to 30 to 90 percent solids content when filtered or centrifuged. The resulting sludge is quite stable, and no leachate problems are anticipated.

The process is now in use at Clarostat, a plating shop, to remove heavy metals from the wastewater before discharge. Metals can be recovered from ISX sludge, but the process requires either chemical treatment or incineration. Currently, only gold is recovered from ISX sludge.

Immiscible Organic Solvents

The use of immiscible organic solvents for extraction of heavy metals from waste effluents is gaining industrial importance, particularly outside the United States. In Sweden, four solvent extraction processes have been developed, and at least two are applied in large treatment plants for recovery of metals from industrial waste.

A prototype of a patented solvent-based process for metal recovery was demonstrated by EPA on a chrome plating line. The system uses a two-stage solvent spray rinse followed by a single aqueous immersion rinse. The metal value is extracted from the solvent and returned to the plating bath, and the solvent is recycled continuously. The system has resulted in significant savings in operating, chemical, and water costs. At this time, the system is still in the pilot stage of development.

Centralized Waste Treatment

The concept of centralized treatment is one in which industrial metal finishers in a regional area share the costs of operation and construction of a waste treatment plant to handle metal finishing wastewater. Cost sharing is based on volume, concentration, and types of pollutants.

The major advantage of centralized waste treatment is that the investment required for a single large facility is much less than that associated with installing a treatment plant at each company. Other advantages include the ability to store and use selected wastes as treatment reagents, waste segregation that would facilitate feasible resource recovery, and lower sludge disposal and operating costs.

EPA recently evaluated a centralized waste treatment plant in Western Germany, and has initiated an evaluation of the economic potentials and applicability of this concept in the United States.

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Appendix A. Drag-Out Recovery Cost Reduction Worksheet

The worksheet is intended to lead the user through the analysis required to determine the potential cost reduction achievable by recovery of plating solution drag-out.

Table A-1 illustrates the procedure, and Table A-2 is the worksheet with blanks unfilled.

In the tables the annual operating cost (C.14) represents only the cost of raw material losses, bath heating, pollution control, and waste disposal for a plating line. Comparing the operating cost associated with different investment options, will indicate the relative economy of the different options.

Other items to consider in a complete cost comparison include the labor and investment associated with the modifications. Table 5 of this report shows a cost analysis for determining the total annual cost of a waste treatment system. The same procedure can be used to determine total annual cost for drag-out recovery options.

Table A-1.

Worksheet Completion Procedure

A. Plant conditions to be measured	
1. Drag-out rate (gal/h)	1.5 gal/h
2. Plating tank temperature (°F)	150° F
3. Plating tank air agitation rate ($stdft^3/min$)	0
4. Plating tank surface area (ft^2)	36 ft^2
5. Number of rinse tanks	4
6. Dissolved solids concentration in plating tank (mg/l)	260,000 mg/l
7. Dissolved solids concentration in final rinse (mg/l)	50 mg/l
8. Plating solution composition	
$NiSO_4$ =	1.66 lb/gal
$NiCl_2$ =	0.34 lb/gal
Boric acid =	0.40 lb/gal
B. Cost factors for each plant	
1. Plating solution value ($/gal)	
$NiSO_4$ (1.66 lb/gal × $1.21/lb)[a] =	$2.01/gal
$NiCl_2$ (0.34 lb/gal × $1.57/lb)[a] =	$0.53/gal
Boric acid (1.40 lb/gal × $0.176/lb)[b] =	$0.07/gal
Total =	$2.61/gal
2. Water use and sewer changes	$1.10/1,000 gal
3. Energy cost for plating tank heaters	$3.00/$10^6$ Btu
4. Annual operating hours	3,600

Table A-1.

Worksheet Completion Procedure—Concluded

C. Operating cost estimation for rinse and recycle system (Figure 31)	
1. Surface evaporation rate (gal/h)[c] (0.14 gal/h-ft^2) × 36 ft^2	5.04
2. Recycle rinse ratio (surface evaporation rate/drag-out rate) or (C.1/A.1)	3.36
3. Number of countercurrent rinse tanks in recovery rinse	2
4. Percent recovery of drag-out (from Figure 32)	94
5. Concentration of drag-out from recovery rinse (mg/l) $C_r = 0.06\ C_p$ (from Figure 32)	15,600
6. Number of countercurrent rinse tanks in final rinse	2
7. Dilution ratio in final rinse $\frac{C_r}{C_f} = \frac{15{,}600}{50}$	312
8. Rinse ratio in final rinse (from Figure 27)	18
9. Rinse water requirements in final rinse; gal/h (rinse ratio × drag-out rate) or (C.8 × A.1)	27
10. Drag-out chemical losses ($/h) (drag-out rate) × (plating solution value) × (100 − percent recovery/100) or (A.1 × B.1) × [100 − (C.4/100)]	$0.23/h
11. Rinse water use cost ($/h) (water use rate × cost factor) or (C.9 × B.2)	$0.035/h
12. Bath heating load due to surface evaporation, Btu/h; (5.04 gal/h) × (8,300 Btu/gal)[d]	41,800 Btu/h
13. Heating load cost ($/h) (C.12 × B.3)	$0.125/h
14. Annual operating cost ($/yr) (C.10 + C.11 + C.13) × B.4	$1,404/yr

[a]From Table 10.

[b]From Table 1.

[c]From Figure 29. For aerated baths use Figure 28.

[d]From page 36. For aerated baths use Figure 30.

Table A-2.

Cost Reduction Worksheet

A. Plant conditions to be measured	
1. Drag-out rate (gal/h)	
2. Plating tank temperature (°F)	
3. Plating tank air agitation rate ($stdft^3/min$)	
4. Plating tank surface area (ft^2)	
5. Number of rinse tanks	
6. Dissolved solids concentration in plating tank (mg/l)	
7. Dissolved solids concentration in final rinse (mg/l)	
8. Plating solution composition	
B. Cost factors for each plant	
1. Plating solution value ($/gal)	
2. Water use and sewer changes	
3. Energy cost for plating tank heaters	
4. Annual operating hours	

Table A-2.

Cost Reduction Worksheet—Concluded

C. Operating cost estimation for rinse and recycle system (Figure 31)	
1. Surface evaporation rate (gal/h) _____	
2. Recycle rinse ratio (surface evaporation rate/drag-out rate) or (C.1/A.1)	
3. Number of countercurrent rinse tanks in recovery rinse	
4. Percent recovery of drag-out (from Figure 32)	
5. Concentration of drag-out from recovery rinse (mg/l) _____ (from Figure 32)	
6. Number of countercurrent rinse tanks in final rinse	
7. Dilution ratio in final rinse $\frac{C_r}{C_f}$ or (C.5/A.7)	
8. Rinse ratio in final rinse (from Figure 27)	
9. Rinse water requirements in final rinse; [gal/h (rinse ratio × drag-out rate) or (C.8 × A.1)]	
10. Drag-out chemical losses ($/h) (drag-out rate) × (plating solution value) × (100 − percent recovery/100) or (A.1 × B.1) × [100 − (C.4/100)]	
11. Rinse water use cost ($/h) (water use rate × cost factor) or (C.9 × B.2)	
12. Bath heating load due to surface evaporation (Btu/h) _____	
13. Heating load cost ($/h) (C.12 × B.3)	
14. Annual operating cost ($/yr) (C.10 + C.11 + C.13) × B.4	

This report has been reviewed by the Industrial Environmental Research Laboratory, U.S. Environmental Protection Agency, Cincinnati OH, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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